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Secretary-Treasurer.....H. E. Simmons

Vol. III October, 1930 No. 4

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RUBBER CHEMISTRY AND TECHNOLOGY

RUBBER CHEMISTRY AND TECHNOLOGY is published quarterly under the supervision of the editors representing the Rubber Division of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

RUBBER CHEMISTRY AND TECHNOLOGY may be obtained in one of three ways:

(1) Any member of the American Chemical Society may become a member of the Rubber Division upon payment of the dues ($2.00) to the Division and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(2) Any one who is not a member of the American Chemical Society may become an Associate Member of the Rubber Division (and also a member of his local group if desired) upon payment of $4.00 per year to the Treasurer of the Rubber Division, and thus receive RUBBER CHEMISTRY AND TECHNOLOGY.

(3) Companies and Libraries may subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at a subscription price of $6.00 per year.

All applications for regular or for associate membership in the Rubber Division with its privilege of receiving this publication, all correspondence about subscriptions, back numbers, changes of address, and missing numbers and all other information or questions should be directed to the Secretary-Treasurer of the Rubber Division, Professor H. E. Simmons, Easton, Pennsylvania, or University of Akron, Akron, Ohio.

Rubber Division Activities

H. E. SIMMONS, Secretary-Treasurer of the Rubber Division of the American Chemical Society

The Rubber Division of the American Chemical Society

Officers

Chairman.....H. A. WINKELMANN
Vice-Chairman.....E. R. BRIDGWATER
Secretary-Treasurer.....H. E. SIMMONS
Executive Committee....STANLEY KRALL, G. K. HINSHAW, N. G. MADGE, D. J. BEAVER, H. F. PALMER
Sergeant-at-Arms.....E. NAHM

Minutes of the Rubber Division Meeting Held in Cincinnati

The Fall Meeting of the Rubber Division of the American Chemical Society was called to order in Room 22, Library Building of the University of Cincinnati, at 9.20 A.M., Wednesday, Sept. 10, 1930.

One hundred and fifty members were in attendance at this meeting. Stanley Krall, Chairman of the Division, appointed the following Resolution Committee: C. R. Boggs, E. R. Bridgwater, H. F. Palmer. The Nominating Committee consisted of C. C. Curtis, L. B. Sebrell, J. Harvey Doering, H. J. Conroy, H. E. Simmons.

The following program of papers was then presented: W. B. Wiegand, "Notes on the Carbon Flame;" H. A. Winkelmann and E. G. Croakman, "Water Absorption of Rubber Compounds;" D. J. Beaver and J. W. Mackay, "Reënforcing Action of Pigment Mixtures on Rubber Compounds;" A. M. Finley and M. J. DeFrance, "The Effect of Increasing Gas Black Loading on Flex Fatigue Resistance as Determined on the Goodyear Flexing Machine;" Paul C. Jones and David Craig, "The Behavior of Antioxidants in Rubber Stocks Containing Copper;" J. McGavack and J. S. Rumbold, "The Determination of the p_H of Ammonia Latex by (I) a Colorimetric Method; (II) the Glass Electrode;" Henry F. Palmer and George W. Miller, "Determination of Alkalinity of Reclaimed Rubber;" J. H. Howey, "Hard Spots in Vulcanized Rubber Compounds;" E. Karrer, "The Modified Balance for Approximate and Quick Weighing;" George J. Albertoni, "New Autographic Rubber-Testing Machine;" S. H. Hahn and E. O. Dieterich, "Graphical Tensile-Testing Machine for Rubber Threads;" A. F. Hardman, W. L. MacKinnon, and S. M. Jones, "Kelly Abrasion Machine;" A. A. Somerville, "Report of Physical Testing Committee." Business Meeting. Divisional Dinner, Hotel Gibson, 6.30, September 10th.

The Divisional dinner was held Wednesday evening, September 10th at 6.30 P.M. in the Ball Room of the Gibson Hotel. Bill Whitcomb acted as toastmaster and the entertainment was furnished by stars from the Studio of WLW under the direction of Edward A. Byron with Robert Brown as master of ceremonies. Souvenirs were given by the Godfrey L. Cabot Company, General Atlas Carbon Company, and Federal Color Laboratories, Inc.

The Committee who made the arrangements for the dinner consisted of C. W. Sanderson, *Chairman*, Walter H. Juve, and Harold Gray. One hundred and fifty-five people were in attendance at the banquet.

At the business meeting of the Division held Thursday, September 11th, Dr. A. A. Somerville, Chairman of the Physical Testing Committee, made the following report, which by motion was accepted:

"At a meeting of the Committee held prior to the last meeting of the Rubber Division six months ago, it was considered desirable that Rubber Testing Laboratories should be made acquainted with the 'Outline of Tentative Standard Laboratory Procedure for the Preparation and Physical Testing of Rubber Samples,' and that laboratories should be rated in order that they might know how well they are equipped for complying with the Standard Laboratory Procedure, and encouraged to conform more closely with that procedure.

"The Committee is not being financially supported by the Rubber Manufacturers Association of America this year. Accordingly the three Chemical Supply Companies represented on the Committee volunteered the services of several of their men to rate laboratories wherever they were invited to do so. The Secretary of the Rubber Division addressed a circular letter to about two hundred and fifty rubber testing laboratories on this subject. Requests were received from fourteen laboratories asking for rating. Nine of these were from rubber goods manufacturers; one reclaimer; two chemical suppliers and two automobile manufacturers.

"It would appear that there is no great demand for a rating of laboratories.

"It might be added that the fourteen laboratories visited received an average rating of 51% toward compliance with the Tentative Standard Procedure. No other work has been done by the Committee during the past six months."

The Secretary-Treasurer submitted the following report, which by motion was accepted and ordered made a part of the permanent records of the Division:

Balance in Bank at Atlanta Meeting		$1579.39
Dues and subscriptions		280.17
		$1859.56
Expenditures		
Expenses of Secretary to the Atlanta Meeting	$ 83.50	
Stenographic services	90.00	
India Rubber World—Reprints	88.66	
Palmerton Publishing Company	49.52	
Mack Printing Company	10.46	
Ben Franklin Printing Co	13.75	
University of Akron—postage, telegrams, and office supplies	23.36	
Translations	287.29	
Refunds	4.00	
Correction of $0.08—foreign drafts and checks	0.08	650.62
In bank September 8, 1930		$1208.94

The nomination Committee presented the following members for the various offices: *Vice-Chairman:* E. R. Bridgwater, H. F. Palmer. *Secretary-Treasurer:* H. E. Simmons. *Sergeant-at-Arms:* Lester W. Brock, Ed Nahm. *Executive Committee:* N. G. Madge, J. N. Street, F. W. Frerichs, W. N. Jones, G. K. Hinshaw, D. J. Beaver.

The results of the election are as follows: *Chairman*, H. A. Winkelmann; *Vice-Chairman*, E. R. Bridgwater; *Secretary-Treasurer*, H. E. Simmons; *Sergeant-at-*

Arms, Ed Nahm; *Executive Committee:* G. K. Hinshaw, N. G. Madge, D. J. Beaver, H. F. Palmer (next highest for Vice-Chairman), Stanley Krall (Ex-Chairman).

By motion meeting adjourned.

H. E. SIMMONS, *Secretary-Treasurer*

Minutes of the Executive Committee

Following the adjournment of the Division meeting the newly elected Chairman, Dr. H. A. Winkelmann called a meeting of the Executive Committee in the Library at the University of Cincinnati.

The following members were present: Dr. H. A. Winkelmann, E. R. Bridgwater, H. F. Palmer, Stanley Krall, H. E. Simmons.

The Secretary presented to the Executive Committee the plans worked out by W. F. V. Cox of the Institution of the Rubber Industry and H. E. Simmons, Secretary of the Rubber Division, for the interchanging of publications of the two Societies, as follows:

The members of the Institution of Rubber Industry are eligible to subscribe to RUBBER CHEMISTRY AND TECHNOLOGY at a subscription price of 17 shillings, the application for such subscription to be sent directly to the Secretary, H. E. Simmons; and the members of the Rubber Division of the American Chemical Society may subscribe for the *I. R. I. Transactions* for $4.00 per year by making application directly to W. F. V. Cox, Secretary of Institution of the Rubber Industry.

Attention of the Executive Committee was called to the resignation of Dr. A. A. Somerville as Chairman of the Physical Testing Committee, as follows: "Will you kindly transmit to the Chairman of the Rubber Division of the American Chemical Society my resignation as Chairman of the Physical Testing Committee."

Meeting adjourned.

H. E. SIMMONS, *Secretary-Treasurer*

Report of the Treasurer of the Rubber Division

Last Treasurer's report June 1st		$1352.85	
Dues and subscriptions		168.47	
			$1521.32
Expenditures:			
Ben Franklin Printing Company	$ 6.75		
Mack Printing Company	3.30		
Translations	175.00		
Postage, supplies, and telegrams	9.07		
Stenographic services	60.00		
Reprints from *India Rubber World*	54.26		
Refund	4.00		
		$312.38	312.38
Bank balance as of Sept. 4, 1930			$1208.94

H. E. SIMMONS, *Secretary-Treasurer*

New Books and Other Publications

Rubber-Textile Symposium. Reprinted from *The Rubber Age*. Published by the Binney & Smith Company, 41 East 42nd Street, New York City. June, 1930. 36 pp. For free distribution.

"In rubber technology, as elsewhere, some of the richest finds have been made by those who have dared to paddle more than their own canoe!" says W. B. Wiegand, Chairman of the New York Rubber Group, in a foreword to these papers. "The art and the science of the textile technologist have added much and will add more to the fullest understanding and the most economical employment of rubber products." The six papers, all of which were presented at a New York Group meeting on December 16, 1929, cover the use of rubber-fabric combinations in footwear, in balloon materials and in transmission belting, the use of rubber-pyroxylin textile combinations, the strength and stretch of double texture rubber goods, and the effect of rubber proofing process on the tensile strength of fabric, while the authors include Arnold R. Davis, R. P. Dinsmore, K. E. Burgess, W. L. Sturtevant, D. P. Weisberg, T. M. Knowland, and A. R. Lewis. [From *The Rubber Age* of New York.]

Bus and Truck Tubes. Published by the Rubber Chemicals Section, E. I. du Pont de Nemours & Company, Wilmington, Del. 1930. 8 pp. For free distribution.

The authors of this laboratory report are of the opinion that in the case of bus and truck tires an aging test in air at 90 degrees or 100 degrees Centigrade while the stock is under tension produces the best approximation to the type of deterioration that occurs in service. The paper gives the results of a series of aging tests under 50 per cent elongation at 100 degrees Centigrade, including a comparison of several anti-oxidants and anti-oxidant combinations in a typical high grade truck tube compounded with zinc oxide. [From *The Rubber Age* of New York.]

La Coloration du Caoutchouc. By F. Jacobs. Published by La Revue Générale du Caoutchouc, 18 Rue Duphot, Paris, France. 1930. 64 pp. 12 francs.

The coloring of rubber and rubber products has always been a difficult problem for technologists. M. Jacobs has organized concisely all information available to him on the various types of colors used in the industry in this illustrated volume. His work, however, was prepared too soon to include the latest developments in rubber dispersed colors. [From *The Rubber Age* of New York.]

Progress of Applied Chemistry. Published by the Society of Chemical Industry, London, England. 1930. 708 pp.

In the 14th volume of this British society's annual reports, the chapters on rubber are written by Dr. H. P. Stevens and W. H. Stevens. In a section on planting, the authors discuss the Liberia and Amazon Valley rubber growing projects and also make an interesting comparison of routine methods employed on Malayan and Javanese estates, while in their latex section there is a discussion as to the form in which the resins exist in latex and of the behavior of these resin globules. Other subjects treated briefly are raw rubber, plasticity, vulcanized rubber, properties of vulcanized rubber, accelerators and anti-oxidants, compounding ingredients, colors, reclaim, aging and oxidation, testing and analysis, apparatus and manufacture, and applications. [From *The Rubber Age* of New York.]

Periodical Pamphlet No. 3 of the Metallgesellschaft (Frankfort-am-Main). April, 1930. This finely edited pamphlet contains a contribution to the history

of the Revertex process by E. A. Hauser, who in very clear style describes the origin of this process, investigations to which it has led, and its practical and industrial applications. The article by Hauser is illustrated with eleven excellent photographs. The publication also contains articles on other technical subjects. [From *Caoutchouc and gutta-percha.*]

American Standards Year Book. Published by the American Standards Association, 29 West 39th Street, New York City. 1930. 104 pp. For free distribution.

The importance of standardization to industry is well known, and this annual sums up the projects to that end undertaken by the association. Of particular interest are the standard for cotton rubber-lined fire hose and the safety code that is proposed for rubber machinery. [From *The Rubber Age* of New York.]

Annual Report, 1929. Published by the Rubber Research Institute of Malaya, Kuala Lumpur, F. M. S. 1930. 100 pp. $1 (Malaya).

Considerable progress was made in the fourth year of the Rubber Research Institute of Malaya, despite important changes in the personnel and shortage of staff. Individual reports are made in this volume by the director, the soils division, botanical division, pathological division, chemical division, bacteriologist, and the experimental station, in addition to which the annual accounts are presented in full. [From *The Rubber Age* of New York.]

International Control of Raw Materials. By Benjamin Bruce Wallace and Lynn Ramsay Edminster. Published by the Brookings Institution, Washington, D. C. June, 1930. 494 pp. $3.50.

That the unequal distribution of raw materials among the nations of the world has given rise to some of the most difficult problems in economics and international relations is appreciated only too well by those in the rubber industry. Appropriately, therefore, the authors of this volume devote a 47-page chapter exclusively to the British export restrictions on rubber and include in a 20-page appendix reports of the committee, headed by the late Sir James Stevenson, which drafted the restriction act. Other restrictive efforts considered in full detail are the Chilean control of sodium nitrate, the Japanese camphor monopoly, the Franco-German potash combine, the Brazilian valorization and control of coffee, and the Canadian embargoes on pulpwood. Dr. Wallace and Mr. Edminster cannot find that past restrictive measures have been satisfactory to all parties concerned, but it is doubtful whether their suggestion of handling the problem through a commercial division of the Permanent Court of International Justice would prove to be more practicable. [From *The Rubber Age* of New York.]

"Fünfsprachiges Worterbuch für den Gummiwarenhandel." Published by Union Deutsche Verlagsgesel!schaft, Zweigniederlassung Berlin, Germany. Board covers. 140 pages.

This five-language dictionary (German, French, English, Italian, and Spanish) for the rubber trade attempts to fill a need which undoubtedly exists. Unfortunately, however praiseworthy the effort may be, the numerous errors of various kinds in which the little compilation abounds detracts considerably from its usefulness. A glance over the English equivalents shows many mistakes like "eyes-bath;" misprints are far too frequent; while expressions like "dolls sucking," "stuffs for gaberdines," "beltings adhesive fad," "disks cutting," "hoses-making machine," "eyes-dropping glass," "rolling cover," "bacon rubber," etc., leave entirely too much to the imagination. [From the *India Rubber World.*]

A Survey of Recent Literature on the Chemistry of Rubber

Abstracts of Articles Pertaining to the Chemistry of Rubber Which Have Appeared in Foreign and American Journals

The following abstracts are reprinted from the July 10 and 20, Aug. 10 and 20, and Sept. 10 and 20, 1930, issues of *Chemical Abstracts* and, with earlier and succeeding issues, they form a complete record of all chemical work published in the various academic, engineering, industrial, and trade journals throughout the world.

Research and production of the Rubber Service Laboratories Company. R. L. SIBLEY. *Ind. Eng. Chem.* **22**, 552–4(1930). C. C. DAVIS

Toxic substances in the rubber industry. VIII. Chromium and its compounds. P. A. DAVIS. *Rubber Age* (N. Y.) **26**, 541–2(1930); cf. *C. A.* **24**, 1763.—Though poisonous, Cr and its compds. can be safely used with proper control. Systematic involvement is rare, but skin and mucous membrane involvements are common. **IX. Amyl acetate and the amyl radical.** *Ibid* 657–8; cf. *C. A.* **24**, 524.—The toxic effects of Am derivs. can be minimized by proper ventilation, supervision and periodic examns. There is a definite change in the blood over long periods of time, and there is no sp. treatment except removal and aeration. **X.** *Ibid* **27**, 145–6.—The various effects of acetone are described. It can be safely used with good ventilation, and is much less toxic than other common solvents. There are no characteristic blood findings to serve as diagnosis, nor is there a sp. medication. C. C. DAVIS

Chemist's report for 1928. T. E. H. O'BRIEN. *Seventh Rept. Exec. Comm. Rubber Research Scheme (Ceylon) Proc. 1928*, 12–7(1929); *Rev. Applied Mycol.* **8**, 600.—Two apparently identical samples of blanket crepe rubber were prepared in January, 1928, from one batch of latex coagulated with AcOH and with AcOH contg. *p*-nitrophenol, resp., in the proportion of 1–4000 parts of dry rubber. After 12 months' storage, the rubber not treated with *p*-nitrophenol was badly mottled and showed surface mold, whereas the other was quite satisfactory. The addn. of this proportion of *p*-nitrophenol is recommended when the blanket crepe is likely to be stored for some time or sold in a distant market. O. E. SHEPPARD

Notes on streakiness in blanket crepe. T. E. H. O'BRIEN. *Trop. Agr.* (Ceylon) **74**, 71–4(1930).—It is frequently stated that Fe in the water used to dil. and coagulate latex discolors crepe rubber. To test the truth of this statement crepe was made with pure water, and water contg. various forms of Fe. When the water contained 10 p. p. m. of $FeCl_3$, 10 p. p. m. of $FeSO_4$ or 13 p. p. m. of finely divided Fe rust, no appreciable discoloration occurred. A. L. MEHRING

Chemical adsorption studies of rubber fillers and rubber compounds. I. G. FROMANDI. *Kautschuk* **6**, 27–30(1930).—The object of the expts. was to develop a method for evaluating the behavior of blacks in rubber by their power of adsorption. It was assumed that the chem. and phys. nature of the surface of all blacks was the same. The blacks were agitated with dil. AcOH of different concns. and the adsorption equilibria detd. The results are tabulated as isothermal concn.-adsorption curves. The curves show, in general the characteristic trend of adsorption, and conform to the formula of Freundlich: $x = K(c - x)n$. The isotherms of the various blacks (gas blacks, oil blacks, inactive black) showed distinctly different trends. The log form of the equation: $\log x = \log K + n/[\log (c - x)]$ shows the characteristic differential powers of adsorption still more clearly, and affords a means of detg. the numerical value of K and n, and the K values are a good criterion of the value of the blacks, as shown by the following K values obtained: gas black No. 1, 3.25; gas black No 2, 2.90; oil black No. 1, 1.10; oil black No. 2, 0.74; inactive gas black, 0.26. To correlate the various blacks in the lab., it is sufficient to obtain a factor expressing the power of adsorption in a definite concn. of AcOH, *e. g.*, in 1 *N* AcOH. The interpretation of the results with respect to the technical behavior of the blacks in rubber is to appear in a subsequent paper. C. C. DAVIS

A spiral model of rubber. H. FIKENTSCHER AND H. MARK. *Kautschuk* **6**, 2–6 (1930).—The "primary valence chain" model of rubber of Meyer and Mark (cf. *C. A.* **23**, 1524) is improved and developed structurally and with its aid the important phys. and chem. properties of rubber are explained. *Elasticity.*—The effective force which causes the extended chains to recoil upon release into spirals is the residual valences of the double bonds. If the temp. of a stretched crystallite at 0° is raised, internal van der Waals' forces parallel to the direction of stretching become active and first one chain and then another moves out of range of the forces of attraction of adjacent chains and contracts under the influence of internal cohesive forces, causing loss of cryst. structure. *Work of stretching.*—To overcome the van der Waals' forces, work must be expended during stretching, and this work is reversible. The elongation curve is S-shaped because up to 80% a great force is required to open the spirals on account of the double bonds lying close together. Cooling takes place; the spirals are successively elongated into the chain and crystn. is accompanied by a positive heat tone. Finally it requires a large amt. of work to elongate the crystallites. *Heat tone during stretching and release.*—Warming above the first steep part of the elongation curve is only in small part an equiv. of the work of stretching, and for the greater part is heat of crystn. (cf. Hock, *C. A.* **18**, 3490). The heat tone on stretching comprises: (1) a neg. tone to overcome the forces of attraction of the residual valences of the double bonds; (2) an irreversible heat of friction which is the equiv. of the plastic work of elongation; and (3) a heat of crystn. which is set free when the elongated chains are orientated in the ordered crystal lattice. In conjunction with the heat of friction, this heat of crystn. is responsible for the strong pos. heat tone during stretching and the cooling effect upon release. *Sp. vol.*—A diminished sp. vol. accompanies the more compact and more orderly arranged lattice of stretched rubber. *X-ray interferences and double refraction.*—The interference and refraction phenomena observed on stretching rubber result from a gradual slipping of the chains past each other. *Permanent elongation.*—The increasingly irreversible elongation which accompanies an increasing period of elongation depends upon the chains slipping past one another. *Swelling and solvation.*—The mols. of swelling agent penetrate among the coiled spirals, sat. the residual valences of the double bonds and cause a stretching of the primary valence chains. *Vulcanization.*—This brings about a union of the chains through S bridges. Soft rubber contains only a few such bridges and the structure is essentially the same as before. Only slipping is inhibited by the bridges, so only swelling instead of soln. takes place. In hard rubber there is an intricate network of chains. *Satn. of the double bonds with halogen or H halide.*—By satn. the active force which coils the springs is removed and progressive loss of elasticity ensues. *Hydrogenation of the double bonds.*—Quant. hydrogenation cannot be accomplished, probably because of partial satn. of the double bonds among themselves or by the solvent. *Cyclicization.*—This, on the contrary, is easy, for the double bonds superposed on one another in the spirals are satd. mutually, with formation of true C—C bonds. There are other properties of rubber which agree with the proposed model, *e. g.*, the *max. resistance to tearing in the direction of the chains.* The *difference between sol- and gel-rubber* is explained on the assumption that Et_2O as a bad solvent can dissolve only the free rubber chains, while the more entangled chains remain behind in swollen but intact structural form.

C. C. DAVIS

A spiral model of rubber. F. KIRCHHOF. *Kautschuk* **6**, 31–3(1930).—Attention is called to earlier work of K. (cf. *C. A.* **16**, 1885, 4363) which led to the development of a spiral model essentially the same as that of Fikentscher and Mark (cf. preceding abstr.).

C. C. DAVIS

The allies of rubber and their influence on rubber products. R. M. FITZPATRICK. *Proc. Soc. Chem. Ind. Victoria* **29**, 275–87(1929).—A general, semi-popular review.

C. C. DAVIS

Rubber-pyroxylin textile combinations. K. E. BURGESS. *Rubber Age* (N. Y.) **27**, 140–1(1930).—Descriptive. C. C. DAVIS

Technology of rubber-textile combinations, with reference to transmission belting. W. L. STURTEVANT AND D. P. WEISBERG. *Rubber Age* (N. Y.) **27**, 141–3(1930).—Factory data show the characteristics of different types of duck in the frictioning operation and the resulting quality of the belts. C. C. DAVIS

Rubberizing balloon fabric. R. P. DINSMORE. *Rubber Age* (N. Y.) **27**, 139–40 (1930).—A description of the important features of construction and compounding.

C. C. DAVIS

Rubber fabric combinations as used in rubber footwear. ARNOLD R. DAVIS. *Rubber Age* (N. Y.) **27**, 87–8(1930).—A general description. C. C. DAVIS

Some factory problems in tire manufacturing. H. B. UNDERWOOD. *Rubber Age* (N. Y.) **27**, 31–2(1930).—A discussion. C. C. DAVIS

Brinell hardness of metals, rubber and hard rubber. R. ARIANO. *Industria* **43**, 257–63, 281–7(1929).—A general discussion of the math. principles of hardness detns. by the Brinell and Meyer methods. In particular, data are given on hardness detns. of various types of hard rubber. E. I. S.

Reclamation and use of old rubber. K. BING. *Ingenioren* (Copenhagen) **38**, 65–72(1929).—More than $^1/_4$ of the rubber consumption is supplied by reclaimed rubber. Methods of reclaiming and refining old rubber of different kinds are described. E. I. S.

Aging of rubber and its retardation by the surface application of antioxygens. Diffusion process. CHARLES MOUREU, CHARLES DUFRAISSE AND PIERRE LOTTE. *Ind. Eng. Chem.* **22**, 549–51(1930); cf. M. and D., *C. A.* **16**, 3737; **19**, 1126; **20**, 3374; **21**, 2816.—The protective action of the diffusion process, where the antioxygen is applied as a soln. to the surface of the rubber, is shown to be a very effective method by representative tests of vulcanized rubber treated with several antioxygens. It is proved that the antioxygen penetrates into the interior and thus protects the strata of rubber below the surface to a degree commensurate with the diffusion of O. The effect depends to a certain extent upon the solvent. By this method the treatment may be renewed. In using antioxygens, account must always be taken of the fact that antioxygenic catalysis may undergo inversion; *i. e.*, a substance may under certain conditions accelerate oxidation (cf. M. and D., *C. A.* **20**, 3374). Attention is again called to the incorrect term antioxidant instead of antioxygen. Many antioxygens are destroyed by oxidizing agents and are not antioxidants. Rubber (contg. no antioxygen) already exposed to O needs more antioxygen to protect it thenceforth because of the partial destruction of the antioxygen by the perioxides already formed. Ultra-violet light forms O_3 and antioxygens do not protect rubber against this, so an ultra-violet light test is of no significance as a test of antioxygens. C. C. DAVIS

Studies of the aging of vulcanized rubber. X. The relation between degrees of oxidation of vulcanized rubber and the occurrence of the maximum state of acetone extracts. TAKEJI YAMAZAKI AND KAROKU OKUYAMA. *J. Soc. Chem. Ind., Japan* **33**, Suppl. binding 68–72(1930).—The discovery of Y. that the acetone ext. of rubber in the process of aging sometimes increases to a max. and then decreases (cf. *C. A.* **22**, 2684) was considered worthy of further more systematic investigation. Vulcanizates contg. rubber and S alone and others with diphenylguanidine and ZnO in addn. were tested. The vulcanizates were extd. with acetone before aging to accelerate oxidation and to eliminate the effect of free S and resin. The progressive changes in % acetone ext. and in wt. were detd. when the rubber-S samples were aged in air at 70° and the accelerated vulcanizates in air at 70° and 90°. The results are recorded in tables and graphically for the vulcanizates cured to different extents. With both types of mixts. the acetone ext. increased to a max. and then gradually diminished. The max. acetone ext. was reached more slowly with the vulcanizates contg. accelerator. The decrease in ext. after the max. was caused by the partial formation of acetone-insol. substances. Elementary analysis of the aged samples which had previously been acetone-extd. showed that the O content increased progressively with aging. The vulcanizates were extd. with acetone and aged as before. The rate of oxidation was far more rapid but the course of the oxidation was the same. C. C. DAVIS

Preserving rubber, and rendering hardening rubber pliable. BRUÈRE. *J. pharm. chim.* [8], **10**, 196–9(1929).—The treatment suggested applies only to overvulcanized rubber. Heavy refined paraffin oils are used (cf. *C. A.* **21**, 3104; **23**, 4015–6). For preservation, cold application is made; rubber about to harden is rendered supple by applying paraffin oil heated to 110–115°. Imbibing assisted by gently rubbing will take place for several hrs. after the application. About 500 cc. of the oil is used for 5 kg. of rubber articles, which are finally covered with a layer of talc. S. WALDBOTT

The influence of the principal accelerators of vulcanization on the preservation of rubber. R. THIOLLET AND G. MARTIN. *Caoutchouc & gutta-percha* **27**, 14842–9 (1930).—In continuation of the earlier expts. (cf. *C. A.* **24**, 1248) the effect of the same 13 accelerators in the same base mixt. (given in the initial part of the previous paper) on the aging was studied. Combinations of different accelerators were also tested. The characteristic temp. of each accelerator was used for curing each mixt. at 2 cures, a slight "undercure" and a cure beyond that coincident with the best aging. Aging was in air at 70° for 10 days. The results are recorded graphically as curves showing the changes in the ultimate elongation and tensile strength as a function of the time of heating. Designating by *A* the % elongation at rupture and by *C* the tensile strength, *AC* was obtained for each mixt. before and after aging. The following data give the time (min.) of cure, the temp. (steam pressure in kg.) of cure and the % loss in *AC* by aging, resp., with the various accelerators: Zn methyldithiocarbamate (I) 24, 1, 27; 35, 1, 35; tetramethyl-

thiuramdisulfide (II), 8, 2, 51; 15, 2, 56.5; mercaptobenzothiazole (III) 36, 3, 13.5; 70, 3, 31; diphenylguanidine (IV) 64, 3, 51; 100, 3, 82.5; di-*o*-tolylguanidine (V) 56, 3, 86; 110, 3, 96; phenyltolylxylylguanidine (VI) 64, 3, 62; 100, 3, 90; ethylideneaniline (VIII) 40, 2.5, 16.5; 80, 2.5, 36; *p*-nitrosodimethylaniline (VIII) 60, 2.5, 27; 95, 2.5, 47.5; thiocarbanilide (IX) 90, 3, 40.5; 130, 3, 53; anhydroformaldehyde-*p*-toluidine (X) 60, 3, 18.5; 90, 3, 68; anhydroformaldehydeaniline (XI) 72, 3, 15; 100, 3, 42; triphenylguanidine (XII) 68, 3, 42; 110, 3, 56.5; III plus VII, 20, 2, 12; 50, 2, 27.5; III plus IV, 32, 1.5, 15; 60, 1.5, 33; I plus XI, 24, 1, 17; 40, 1, 19.5; Zn isopropylxanthate (XIII) 8, 100, 32; 12, 100, 43. These results lead to the following classification into best, poorer and least desirable, based on *AC* losses of 0–20, 20–40 and above 40%, resp.: (I plus XI, III, VII, XI, X, III plus VII, III plus IV; (2) XIII, I, VIII, IX; (3) II, IV, V, VI, XII. In conjunction with the earlier results, it is concluded that III and VII have very favorable characteristics; *viz.*, medium precocity, sufficiently great activity, long plateau of vulcanization and good aging. Mixts., accelerated with these, age satisfactorily even when considerably overcured. An antioxidant should be used with the accelerators of the 3rd group above. Mixts. accelerated with guanidines age better when loaded than those of the "pure gum" type. C. C. DAVIS

Studies of conditions affecting the vulcanization of rubber. IV. Heat reaction during vulcanization. YUTAKA TOYABE. *J. Soc. Chem. Ind., Japan* **33,** Suppl binding 96–8(1930); cf. *C. A.* **24,** 2326.—Rubber prepd. from latex by acetone was mixed with different proportions of S and cured at 155°. The heat effects during vulcanization were recorded by a differential thermocouple, with 1 contact point in a sealed tube enclosed in the rubber and the other contact in the heating medium of an elec. furnace. The heat tones are shown graphically as a function of the time of heating, and the free and combined S are tabulated. The trends of the curves were the same; each had a max. at 60–70 min. (*i. e.*, independent of the proportion of S); and each decreased asymptotically to the temp. of the medium. The max. heat evolution occurred when about 0.5 of the S had combined, *i. e.*, the ratio: free S/total S was about 0.5, independent of the original proportion of S. This is in contrast to other exothermic reactions, yet the temp. coeff. of vulcanization was normal, *viz.*, about 2. If it is assumed that vulcanization is a chem. reaction and its rate depended upon a disaggregation of rubber micelles, then the rate of S combination is: $dx/dt = K(R - x)(S - x)$ ..... (I), where R is the no. of chem. units of rubber per unit vol. of system, S is the same for S, x is the no. of chem. units of the reaction system chemically combined during time t, and K is the velocity const. Though normally const., R varies with the disaggregation. By calling $r = R - x$ and integrating the equation, it is found that $\int rdt = (1/K)$ log (*total S/free S*) (II). From the start, disaggregation accompanies combination of rubber and S, and when disaggregation ceases, the velocity of combination reaches a max. (equation I). Since heat evolution is proportional to reaction velocity, equation II indicates a rise in temp. which depends only upon the ratio of total to free S and is independent of the time. The exptl. results agree with this. C. C. DAVIS

A short comparison of white fillers, with special reference to pigmentation. T. R. DAWSON. *India Rubber J.* **79,** 315–7(1930).—Rubber-S mixts. contg. various proportions of pigments and fillers (TiO_2, copptd. TiO_2-$BaSO_4$, lithopone, ZnO, ZnS, Mg carbonate, clay, $CaCO_3$ and pptd. Ba_2SO_4) were cured at 153° to their optimum phys. state and were then tested for their phys. properties and were examd. by eye to ascertain their relative degrees of "whiteness." ZnS was the most powerful whitening agent, though it imparted a cream-yellow tone. The next most powerful substance was a pptd. TiO_2-$BaSO_4$ contg. 69% TiO_2, followed by a pptd. TiO_2-$BaSO_4$ contg. 26% TiO_2, then by lithopone, ZnO, amorphous TiO_2, $CaCO_3$, pptd. $BaSO_4$, clay and Mg carbonate. This relative intensity of effect is for the same wt. on the rubber. The samples contg. lithopone darkened on exposure to light, but became white again when returned to darkness. After 3 yrs. of storage in darkness, all samples had become yellow or yellow-brown, with the least discoloration in the vulcanizates contg. ZnO. A bibliography of 43 references dealing with color, particularly "whiteness," is appended. C. C. D.

Aging, hysteresis, melting points, work capacity and mechanical performance of progressively racked rubber. HEINRICH FEUCHTER WITH ERNST A. HAUSER. *Kautschuk* **5,** 194–200, 218–27, 245–50, 276–83(1929); *Gummi-Ztg.* **44,** 1307–8(1930).—The expts. and theories of F. are extended by a study of the aging phenomena of racked rubber. The fact that newly racked rubber is considerably more sensitive to temp. than racked rubber which has been stored for a long time induced F. to carry out a large no. of expts. with the object of detg. whether during storage a noticeable displacement of the "fusion line" (cf. *C. A.* **22,** 3065) follows recovery from racking, whether there is also a residual thermoelastic elongation, or whether on the contrary there is a "permanent elongation." The most important result of this part of the work is the

discovery that racked rubber which has aged has a definite m. p., and that there is an increase in d. of the same order of magnitude as the increase in d. accompanying the original racking. Aging is accordingly a peculiar additional hardening effect which is superimposed on the original hardening effect of racking. This phenomenon is termed *racked aging*, and it has been followed by x-ray examn. The intensity of the interferences of aged racked rubber was considerably stronger than that of newly racked rubber under the same conditions otherwise. This indicates an increase in the number of the elementary particles, just as thermal recovery upon release on standing causes, to a lesser degree, a disorientation. The expts. also prove that aged racking involves an increase in the degree of the original racking, which as judged by x-rays is similar in character to the original racking. The fact that in aged racking one is dealing with a substance with a definite m. p. must be surprising in a substance which *a priori* is a typical example of a colloid; yet m. p. is a criterion of a crystalloid. Furthermore, the fact that only upon aging does the product become homogeneous is difficult to explain unless the non-rubber components exert an inhibitory action. Expts. showed, however, that, under certain conditions, raw rubber which has just been racked shows a well-defined m. p., and the expts. as a whole indicate that the attainment of a sharp m. p. does not depend so much upon the chem. purity as upon the uniformity of the elastic aggregation or the state of combination. It was proved that "unsatd." racking (low degrees of racking) becomes thoroughly "satd." on aging. It was then important to ascertain the effect of aging on higher degrees of racking. No such extensive change in the degree of satn. took place on aging, nor was there any contraction in vol. X-ray examn. in this part of the work showed that, although at 600% racking marked changes took place on aging, at 1200% there was no appreciable change on aging, since in each case the interferences disappeared at approx. 44–5°. On the contrary at 2000% racking the interferences again disappeared distinctly earlier in the thermal recovery upon release of newly racked rubber. A theoretical concept of all the phenomena concerned with the elastic state is not possible at present, but there is an analogy between the resilient energy of Wiegand and the work capacity of Becker. A discussion follows of the possibilities inherent in the concept of internal and external thermal work capacity of the racked state, when expressed as thermal work graphically as the surface enclosed by the fusion line of racking and the coördinates. There is then a review of earlier investigations of racking phenomena, progressive racking and aged racking in terms of energetics, with a discussion of the physics and chemistry of racking. Progressive racking allows the differentiation and demarcation of several elastic regions. One region lies at about 45–50°, and above this temp. range there is neither recovery from racking nor racking capacity. The lower limit is at about —8°. In these intervals pure racking with a sharp m. p. can be distinguished from racking hysteresis with fusion ranges. They include the region of the purely elastic state, which lies at about 16–34°. Above this temp. there is the region of heat hysteresis, while below 16° is the region of cold hysteresis. In neither region can pure racking be demonstrated. It is clear that the region of pure racking is the most important from the point of view of elasticity. It may be assumed that a sharp m. p. is evidence of a purely chem. reaction, so that the purely elastic change of state signifies simple thermodynamic reactivity. There follows a discussion of the most recent results of work on surface forces and of their possible relations to the structure of racked rubber; it is assumed that the latter is composed of gigantic joined palisades into a single compact structure. The forces of adhesion and cohesion probably have an elastic function, but polar chains perpendicular to the surface do not explain the structure, for the isotropic elastic link structure is not oriented definitely and is vectorially equiv. It is proved that to ascertain the strength, it is necessary to know not only the work performed but also the time factor. Numerous different expts. indicated that rubber is structurally the same whether it is elongated slowly or rapidly, but not independent of whether it is warmed at 50° for 1 min. or for 1 hr. In a crit. discussion of the structure of rubber, emphasis is laid on the importance of a study of racking as an explanation of the structure of rubber, since the polarization microscope still gives evidence of double refraction when the x-ray interferences have long since vanished. The cylindrical structure suggested by Wiener is necessary to explain pure racking. Concepts and definitions of the chemistry of rubber have so far been inadequate to explain the complex properties of rubber.

C. C. DAVIS

Ultra-accelerators. G. DUMONTHIER. *Rev. gén. caoutchouc* **7**, No. 60, 3–5(1930); cf. *C. A.* **24**, 2915.—The effects of factice, fatty acids, reclaimed rubber and the proportion of S with tetramethylthiurammonosulfide are described, and typical formulas contg. this accelerator are given.

C. C. DAVIS

Effect of rubber substitutes on the physical properties of vulcanized rubber. YOSH-

INOBU KATO. *Repts. Imp. Ind. Research Lab., Osaka, Japan* **11**, No. 1(1930).—The effect of 8 rubber substitutes on the phys. properties of vulcanized rubber has been studied. F. I. NAKAMURA

Heat of swelling of raw rubber (remarks on the work of P. Stamberger and C. M. Blow on the determination of volume contraction). LOTHAR HOCK. *Kolloid-Z.* **51**, 190–1(1930); cf. *C. A.* **23**, 3371; **24**, 2649; Boström, *C. A* **23**, 3371.—S. and B. are alone in their contention that the heat of swelling of rubber is pos. The age, source and previous history of the rubber should be carefully considered in the detn. of the heat of swelling. ARTHUR FLEISCHER

The tensile strength of Java plantation rubber. O. DE VRIES AND R. RIEBL. *India Rubber J.* **79**, 419–20(1930).—Data already published (cf. *India Rubber J.* **75**, 25(1928))on the general quality of Java plantation rubber in 1923–6 are now supplemented by similar data for 1927–9. The results of this routine testing show a steady increase in tensile strength and no indication of any deterioration. Complaints in the rubber industry probably therefore arise from (1) inaccuracies in testing methods; (2) detg. tensile strengths for a standard time of cure instead of a standard state of cure; and (3) the admixt. of native rubber with European estate rubber. The custom in the East of blending lots (with erasure of names) may result in the inclusion of considerable native or Chinese rubber under the name of plantation rubber, with a resulting inferior quality for which European plantations are not responsible. C. C. D.

Artificial rubber. G. KESSEL. *Chem.-Tech. Rundschau* **45**, 135(1930).—The production of artificial rubber as undertaken by I. G. Farbenindustrie is still in its exptl. stages. The intermediate product used in the synthesis is isoprene, which is prepd. from natural carbonaceous materials, including coal and its distn. products. C_2H_2 is recovered from the starting material directly or through CH_4 and is transformed into AcH, which is in turn polymerized to aldol. Through reduction of the latter, 1,3-butyleneglycol is obtained, which yields MeEtCO by partial dehydrogenation at 180–250°. Condensation of this substance with CH_2O_2 results in methyl-2-ketone-2-butanol, which is reduced to 2-methyl-1,3-butyleneglycol, which is, in turn, dehydrogenated to isoprene at 220–250°. Polymerization of isoprene to artificial rubber consists in heating it with water or caustic alkali at 100° in the presence of acids, alkali metals, oxidizing agents, emulsifiers and a buffer system of p_H 4.8–5. J. P.

Colors and pigments for rubber. C. R. HALLE. *Farbe u. Lack* **1930**, 170, 196–8.—A brief review of the functions of pigments in rubber and the types of pigments and dyes used in colored rubber. G. G. SWARD

The coloring of rubber. F. JACOBS. *Rev. gén. caoutchouc* **7**, No. 60, 9–17(1930); cf. *C. A.* **24**, 2915.—The chemistry of $CHCl_3$, N, alizarin, indigo and S dyes is described; methods of analysis are discussed; and the use of colors in the form of lacquers is outlined. C. C. DAVIS

Toxic substances in the rubber industry. XI. Mercaptobenzothiazole. P A. DAVIS. *Rubber Age* (N. Y.) **27**, 249–50(1930); cf. *C. A.* **24**, 3394–5.—Preliminary exptl. evidence indicates that mercaptobenzothiazole is not toxic. The Pb deriv. should, however, be handled with the same care as are other Pb compds. C. C. D.

An inquiry into the inner properties of estate rubber from Java and South Sumatra. R. RIEBL. *Arch. Rubbercultuur* **14**, 223–48(1930). (Summarized in English 249–50.)—To supplement routine data on rubber from the better equipped estates, pale crepe and smoked sheet, from a wide variety of estates throughout Java and South Sumatra, which are not ordinarily examd., were tested in the usual way. Only a small proportion had an abnormally slow or fast rate of vulcanization or an abnormally low tensile strength. Data on slope, viscosity and plasticity also represent a satisfactory condition. C. C. DAVIS

Thermodynamics of rubber. II. Temperature change of rubber under adiabatic stretching. L. S. ORNSTEIN, J. WOUDA AND (MISS) J. G. EYMERS. *Proc. Acad. Sci. Amsterdam* **33**, 273–9(1930).—A heating effect in stretched rubber must be due to hysteresis, because from thermodynamic reasons a substance with a pos. coeff. of elongation shows a cooling effect (cf. *C. A.* **24**, 2635). On this basis, rubber which shows no hysteresis must obey the laws of thermodynamics. A vulcanizate prepd. from rubber 100, S 5, diphenylguanidine 1 and ZnO 3 showed no hysteresis after slow elongation to 250%. From 250 to 370% the recovery followed a different path on the stress-strain coördinates from the path of the original stress-strain relation, and to a certain extent this divergence depended upon the rate at which the stress was released. Above and below this range the path of recovery was the same as the path of increasing stress. This divergence between 250 and 370% elongation was not a result of hysteresis, for however great the stress and for however long it was applied, the rubber regained momentarily its original length upon release. The stress-strain relation above 370% and below 250%

elongation represents 2 different phases of the rubber, and the divergent intermediate curves represent a retardation of the phase change. Because of this, thermodynamic measurements were made below 200% elongation. The formula, $\Delta T = -T \int_0^{\Delta l} [(\delta S/\delta l)_T \times (\delta l/\delta T)_s/(\delta \epsilon/\delta T)_l] dl$, where T is the abs. temp., S the stress, ϵ the energy and $(\delta \epsilon/\delta t)_l$ the sp. heat per cc. at const. length, was tested by detg. the length as a function of the stress at different temps. In this way $(\delta S/\delta l)_T$ and $(\delta l/\delta T)_s$ were calcd. as functions of the elongation, besides which the sp. heat as a function of the elongation was measured. The temps. were 21°, 41°, 61°, 81° and 99°. A new *method for measuring the sp. heat of rubber* was developed. The $(\delta S/\delta l)_T$ and $(\delta l/\delta T)_s$-elongation curves were multiplied by each other and divided by the curve of the sp. heat-elongation curve, which gives: $I = (\delta S/\delta l)_T (\delta l/\delta T)_s/(\delta \epsilon/\delta T)_l$. The area between this curve and the axis was multiplied by T (at which the generation of heat was detd.). To test the thermodynamics, the heat generation was detd. directly by a special method. Up to 150% elongation the calcd. and exptl. values of the heat generation agreed satisfactorily, but above this elongation the exptl. increases in temp. were greater than those calcd. by the thermodynamic formula. This difference is caused by the influence of the second phase of the rubber at 250–370% elongation (*loc. cit.*). The *generation of heat on stretching raw rubber* was also measured. The curve had the same form as the stress-double refractions and the stress-strain curves (cf. O., E. and W., *loc. cit.*). Beyond the transition point, *viz.*, approx. 70% elongation, the rise of temp. increased in direct proportion to the length. Further measurements are planned to ascertain the relation between hysteresis and the development of heat. C. C. DAVIS

The "dry rubber" content of latex from deep and shallow tapping. B. J. EATON AND R. G. FULLERTON. Rubber Research Inst. Malaya, *Quart. J.* **1**, 132–4(1929).—Comparative tapping tests on 2 Malaya estates showed in each case a higher yield of rubber in latex from shallow tapping than from deep tapping, *viz.*, combined av. values of 36.4 and 34.8%, resp. C. C. DAVIS

The identification and quantitative estimation of the yellow pigment of raw rubber. B. J. EATON AND R. G. FULLERTON. Rubber Research Inst. Malaya, *Quart. J.* **1**, 135–48(1930); cf. F., *C. A.* **24**, 1543.—Crepe of an intense yellow color, from the 1st fraction of the regular fractional coagulation process, was dried *in vacuo*, extd. with acetone at room temp., the ext. evapd. *in vacuo*, the residual oil sapond. with 3% alc. KOH, dild. with water and extd. repeatedly with anhyd. Et_2O; the combined exts. were washed with water, dried with $CaCl_2$, filtered and evapd. *in vacuo;* the residual oil was dissolved in petr. ether, extd. with 90% MeOH, the petr. ether layer washed with water, dried with $CaCl_2$ and filtered, which gave a golden yellow soln. This process was based on preliminary tests which showed that a carotenoid was present. A pos. sterol test of the unsaponifiable part of the acetone ext. was obtained by the Whitby method (*C. A.* **17**, 1974). A petr. ether soln. of carotene from carrots was prepd. as a control. Comparative tests of the yellow oils from the rubber and carrots, including soly., $FeCl_3$, concd. H_2SO_4, concd. HNO_3, concd. HCl, NH_4OH, NaOH and CS_2 color reactions, changes on exposure to light, Palmer chromatographic tone, and resistance to bleaching agents gave the same results, showing that carotene is the cause of the yellow color of crepe rubber. According to Palmer (cf. Carotinoids and Related Pigments, the Chromolipoids 1922; cf. *C. A.* **16**, 3492), carotene is closely related to isoprene, and since in mammals carotene is bound to colloidal serum albumin, it may be bound with the protein of latex. For detg. the carotene content of latex, the Palmer method for its detn. in animal tissues was used as a basis. The crepe was extd. with acetone, the ext. was dild. with acetone to a known vol. and its color compared with 0.2% $K_2Cr_2O_7$ in a Kett colorimeter. Data on the comparative colors of carotene and $K_2Cr_2O_7$ solns. have been published by Willstätter and Stoll (Untersuchungen über Chlorophyll. Methoden und Ergebnisse **1913**, 99; cf. *C. A.* **8**, 3565), and these have been converted by Palmer into a graphical form directly applicable to the present work. Four modifications of the procedure were tested: (1) cold extn., no sapon., soln. in acetone; (2) hot extn., no sapon., soln. in petr. ether; (3) hot extn., no sapon., soln. in acetone and (4) hot extn., sapon., soln. in Et_2O. These gave 2.0, 1.8, 2.1 and 1.9 mg. of carotene per 100 g. of 1st fraction crepe. Method (1) is the most convenient. By assuming 35% dry rubber in latex calcns. from the data above indicated 0.1 mg. per 100 g. of latex. The presence of carotene in latex has already been suggested by Frey-Wyssling (*C. A.* **23**, 4845). C. C. DAVIS

Rinmann's green, a powerful reënforcing agent, but not a coloring agent in accelerated rubber mixtures. RUDOLF DITMAR AND KARL H. PREUSSE. *Gummi-Ztg.* **44**,

1842(1930).—The base mixt.: crepe 100 S 3, accelerator 2, Rinmann's green 10, whiting 30 was vulcanized 30 min. at 132° in a press with 19 different com. accelerators, and also without any accelerator. The unaccelerated mixt. was uncured and its color unchanged; in only 5 cases were the vulcanizates green (the others became gray or black), and in most cases the green pigment had an activating action on the accelerator and a toughening effect in the vulcanizates. Rinmann's green cannot be used for S_2Cl_2 vulcanization. C. C. DAVIS

The behavior of pigments during mixing and curing. HARLAN A. DEPEW. *Rubber Age* (N. Y.) **27,** 253–5(1930).—See *C. A.* **23,** 2068; **24,** 749. C. C. DAVIS

Why colors fade on rubber goods. GEO. RICE. *India Rubber World* **82,** No. 3, 63(1930).—Bacteria can destroy some dyes used in rubber goods, and therefore they cause fading on the surface when these goods are exposed under favorable conditions. The only way to combat this is to protect the surface or to expose the goods periodically to sunlight. C. C. DAVIS

The effect of rubber-proofing process on the tensile strength of fabric. A. R LEWIS. *Rubber Age* (N. Y.) **27,** 197–9(1930).—Tensile strength tests were made of representative fabrics before and after rubberizing. The latter process increased the tensile strength in both directions of weaving. The quant. results, including the relative increase in warp and filling, depended upon various factors, including the twist and tightness of yarn, the style of weave, the relation between the style and the weight, the kind of dyeing and the method of rubberizing. The fabrics included sheetings, ducks, drill, flannels and rayons. C. C. DAVIS

The strength and stretch of double texture rubber goods. T. M. KNOWLAND. *Rubber Age* (N. Y.) **27,** 193–7(1930).—An analysis, largely on a mathematical basis, of stress-strain relations in various combinations of plied fabrics, with the end in view of developing methods of calcg. the stretch and strength of any combination and thus of being able to construct rubber-textile products in the most economical way. C. C. DAVIS

Air conditioning in the dipped rubber goods industry. EDGAR MAASS. *India Rubber World* **82,** No. 3, 59–60(1930).—An illustrated description. C. C. DAVIS

Brown bast. Some considerations as to its nature. EDGAR RHODES. Rubber Research Inst. Malaya, *Quart. J.* **2,** 1–11(1930).—Brown bast disease is related closely to the tree reaction of "wound healing" and it obeys the same general laws. A pathol. condition, induced in a few vessels occasionally by tapping, is followed by the deposition of wound gum and the formation of burrs. This deposition of gum is essentially an enzymic process by enzymes normally existing in the tree. The correlation of the disease with enzyme activity and tree vigor explains many obscure fundamental points, *e. g.*, the relation between brown bast trees and dry trees. C. C. DAVIS

Current curing practice. WEBSTER NORRIS. *India Rubber World* **82,** No. 3, 53–5(1930).—A review and discussion. A *nomograph chart of equiv. cures* is included. C. C. DAVIS

Vulcanization by sulfur chloride. ERICH WURM. *India Rubber J.* **79,** 449–51 (1930).—See *C. A.* **24,** 3134. C. C. DAVIS

The history of the "Revertex" process. E. A. HAUSER. *Metallges. Periodic Rev.* No. **3,** 10–6(1930).—An illustrated review. C. C. DAVIS

Physical and physicochemical principles of rubber technology presented in a generally intelligible fashion. LOTHAR HOCK AND HANS J. MÜLLER. *Gummi-Ztg.* **44,** 1644, 1646–7, 1694–6, 1744–5, 1796–7(1930).—A general review and discussion. C. C. DAVIS

Modern developments in control instruments for rubber factories. L. J. D. HEALY. *Rubber Age* (N. Y.) **27,** 308–11(1930).—Illustrated. C. C. DAVIS

Modern developments in instruments for the rubber industry. E. L. STILSON. *Rubber Age* (N. Y.) **27,** 311–4(1930).—Illustrated. C. C. DAVIS

The compressibility of rubber. L. H. ADAMS AND R. E. GIBSON. *J. Wash. Acad. Sci.* **20,** 213–23(1930).—The compressibility of rubber has already been measured at low pressures (cf. Clapeyron, *Compt. rend.* **46,** 208(1858); Lundal, *Ann. Physik* **66,** 741(1898)), but the data in the present paper are the first on its cu. compressibility at high pressures. Three vulcanizates, (1) a rubber-S mixt. contg. 27.4% total S, 0.21% free S and d_{27} 1.149; (2) a rubber-S (90:10) mixt. cured 105 min. at 300°F., of d_{25} 0.990 and (3) a mixt. of crepe 90.75, S 4, tetramethylthiuramdisulfide 0.25, ZnO 5, cured 30 min. at 260°F., of d_{27} 0.990, were tested by a method already described (cf. A., Williamson and Johnston, *C. A.* **13,** 391; A. and W., *C. A.* **17,** 2094). The tabulated results show that the changes in vol. on compression cannot be expressed by a quadratic equation. The compressibility was more like that of a liquid than of a solid, for at low pressures it was very high and it fell off rapidly at higher pressures. With sample (1)

the equation: $y = a + bx + cx^2 + dx^3$ (where $y = -(\Delta V/V_o) \times 10^5$ and $x = (p - 2000)/1000$) represents very well the fractional change in vol. as a function of pressure, but it may be used only as a short interpolation with samples (2) and (3). The hyperbolic equation, $y(x + \text{const.}) = a + bx + cx^2$, is not applicable to vulcanizates (2) and (3), but the equation: $y = A + Bx + C(1 - e^{-Dx})$ is fairly satisfactory, though not so much so as is the cubic equation for the hard rubber. The results are recorded graphically in comparison with the compressibilities of AmOH, K, NaC and steel. The compressibility pressure curves of vulcanizates (2) and (3) are closely akin to the AmOH curve, but show little in common with the curves of NaCl and K. At 0 pressure the compressibility of K is the same as that of soft rubber, but the compressibility-pressure curves are far different (at 12,000 bar the compressibility of rubber is about $^1/_8$ that of K). The compressibility curve of sample (1) is similar to that of K, *i. e.*, more like that of a solid than a liquid. Though at atm. pressure sample (2) was almost twice as compressible as sample (1), it was less compressible at pressures above 5000 b. To show the magnitude of the changes in vol., it is calcd. that 100 cc. of sample (1) at atm. pressure is 85.4 cc. at 12,000 b. and 100 cc. of sample (2) becomes 82.8 cc. The results therefore show in a striking way the great changes in vol. which rubber undergoes when it is subjected to high pressures. C. C. DAVIS

Testing of carbon blacks for rubber. T. L. GARNER. *Chem. Age* (London) **22,** 536 (1930).—A review of analytical methods. C. C. DAVIS

Determination of small quantities of copper in fabrics. A. RUTHING. *Chem.-Ztg.* **54,** 403(1930).—Rubberized fabrics often deteriorate badly and small quantities of Cu accelerate the deterioration. Directions are given for ashing 10 g. of rubberized material, extg. the ash with acids, pptg. CuS with H_2S, dissolving the ppt. in H_2SO_4 and HNO_3 and detg. the Cu colorimetrically after adding an excess of NH_4OH. It is not wise to attempt to remove the rubber coating first but directions are given for removing it with nitrobenzene to find the % Cu in terms of the wt. of uncoated fabric. W. T. H.

Treatment of waste rubber products for the recovery of their components. G. L. GAULTHIER. *Rev. gén. mat. plastiques* **5,** 679–84(1929).—A review of the latest developments, describing more particularly the Tessier-Fouilloux process. A. P.-C.

The determination of total sulfur in rubber. J. G. MACKAY. *J. Soc. Chem. Ind.* **49,** 233–41T(1930).—A survey of the literature on the detn. of total S and systematic expts. on the precision, advantages and shortcomings of the various methods establish the fact that none of the latter is wholly satisfactory. Accordingly, a new method was developed which it is claimed, after tests with 22 different vulcanizates, is superior to any of the previous methods. It is essentially a modification of the Kahane method (cf. *C. A.* **21,** 2817, 4097). Add the sample (0.25 g. of soft rubber, 0.15 g. of hard rubber) in a tube to a mixt. of fuming HNO_3 (10 cc. of d. 1.50), $HClO_4$ (5 cc. of d. 1.54) and Br (0.5 cc.) in a Kjeldahl flask, heat gently until oxidation is complete, boil off excess HNO_3 (if the liquid does not become colorless, cool, add 1–2 cc. of $HClO_4$ and boil again), dil. with water (to 25 cc.) remove (with washing) to a beaker, add 5% aq. $NH_2OH.HCl$ (10 cc.), then 4 *N* KOH until no more $KClO_4$ is pptd., add phenolphthalein (several drops), make alk. with more KOH, filter, make the filtrate acid with 0.1 *N* HCl, boil off all CO_2 (KOH free of carbonates will obviate this), cool (the vol. should not exceed 120 cc.), add dil. benzidine-HCl (300 cc.), let stand 5 min., filter, wash with a min. of 24% EtOH, transfer paper and ppt. to a flask with stopper holding a glass rod, agitate until the whole is disintegrated to a smooth slurry, add phenolphthalein (2 cc.), warm to 50°, titrate with 0.05 *N* NaOH until pink, heat until colorless, add NaOH until again pink, boil to expel CO_2 and titrate until pink. At the end, 1–2 drops of 0.05 *N* HCl should remove the pink and it should not reappear after boiling 2 min. A blank should be made. For rubber mixts. contg. Pb, filter off the $PbSO_4$ remaining after oxidation, det. the H_2SO_4 in the filtrate as benzidine sulfate in the usual way, dissolve the $PbSO_4$ in boiling aq. $NH_4(OAc)_2$, and det. the sulfate in the filtrate as benzidine sulfate. For mixts. contg. Fe_2O_3, reduce the latter to ferrous Fe by $NH_2OH.HCl$ added before the benzidine sulfate pptn. Analyses of 22 mixts. contg. various ingredients showed throughout a good agreement with the results of the Carius method, and with mixts. contg. Ca, Sb and Fe compds. the results were more precise by the new method. The latter, moreover, requires less than 4 hrs. C. C. DAVIS

Crude-rubber statistics. E. G. HOLT. *Ind. Eng. Chem.* **22,** 755–8(1930).—A discussion from the economic point of view. C. C. DAVIS

Rubber-testing laboratory. WEBSTER NORRIS. *India Rubber World* **82,** No. 4, 58–9(1930).—A typical scheme is described and illustrated, with pictures of various types of app. C. C. DAVIS

Toxic substances in the rubber industry. XII. Antimony and its compounds.

P. A. DAVIS. *Rubber Age* (N. Y.) **27**, 367–8(1930); cf. *C. A.* **24**, 3922.—The symptoms of acute and of chronic poisoning by various forms of Sb, and methods of prevention and treatment, are described. C. C. DAVIS

The use of pigments and their dispersion in rubber. PAUL BARY. *Rev. gén. mat. plastiques* **6**, 215–21(1930).—A discussion of the action of pigments in admixt. with rubber, explaining more particularly Blake's theory of the reënforcing action of C black and the effects of fatty (particularly stearic) acids (*C. A.* **22**, 4876; **23**, 4595). A. PAPINEAU-COUTURE

Practical notes on the manufacture of ebonite. RENÉ RÉMY. *Rev. gén. mat. plastiques* **3**, 325–9, 787–91(1927); **4**, 688–91(1928).—This article (which was never finished) deals with the selection and control of raw materials, the technic of the mixing process, baking and vulcanization, finishing and general precautions. It is based on personal experience in the manuf. of ebonite. A. PAPINEAU-COUTURE

The use of crumb rubber and reclaim. PAUL BARY. *Rubber Age* (London) **9**, 176 (1930).—See *C. A.* **24**, 3132. C. C. DAVIS

Notes on defects in smoked sheet and crepe rubber. R. G. FULLERTON. *Rubber Age* (London) **9**, 172–5(1930).—See *C. A.* **24**, 1543. C. C. DAVIS

The fading of colors in manufactured rubber goods. GEO. RICE. *India Rubber World* **82**, No. 4, 57(1930); cf. *C. A.* **24**, 3923.—Conditions are described where fading is illusory. C. C. DAVIS

Laboratory flexing tests as an aid in investigating the pneumatic tire carcass. H. A. DEPEW AND H. C. JONES. *Rubber Age* (N. Y.) **27**, 369–72(1930).—Samples of 6-ply cord belts of various constructions prepd. by the method of Gibbons (*C. A.* **24**, 1543) were tested comparatively for their resistance to flexing, free bending and jerking, the app. for which are described and illustrated. The variables studied included (1) the influence of ply thickness and no. of ends on the resistance to flexing, free bending and jerking and on the stiffness; (2) the influence of the degree of cure on the resistance to flexing, free bending, jerking and plunging and (3) the influence of aging on the resistance to flexing after different cures. The results give in some ways valuable information on tire construction. C. C. DAVIS

Studies in the vulcanization of rubber. I. Thermochemistry of vulcanization of rubber. JOHN T. BLAKE. *Ind. Eng. Chem.* **22**, 737–40(1930).—With the aid of a Daniels calorimeter (cf. *C. A.* **10**, 2419), the heat of vulcanization of rubber by S was detd. over the complete range up to the max. proportion of combined S. The results, which are recorded in tabular and graphical form, show that there is little or no heat interchange of a rubber-S mixt. until after about 6% S has combined. From this point to the complete formation of hard rubber there is a steadily increasing evolution of heat, and this evolution is, in an approx. way above 6%, proportional to the % combined S. This agrees fully with the qual. expts. of Perks, who found that combination of rubber with S was accompanied by a slight heat evolution during the initial stage, which was followed by an energetic exothermic reaction. This latter does not begin until 4–5% S has combined. The max. heat effect at 21% combined S does not, however, agree with the present work. The formation of hard rubber is accompanied by an evolution of 442 cal. per g. of rubber. The significance of this high value is shown by the fact that if no heat were lost during the formation of hard rubber, the temp. would rise 1000°. The av. value of 10 cal. per g. at 10% combined S, calcd. by Williams and Beaver (*C. A.* **17**, 1559), is far below the new value, and the initial heat evolution and final heat absorption are the reverse of the present expts. The formation of soft vulcanized rubber and that of ebonite are apparently 2 sep. and distinct processes, which are very different thermochemically. Further expts. show that during vulcanization with *m*-$C_6H_4(NO_2)_2$ or with Se there is no interchange of heat and in each case only soft vulcanized S is formed. **II. Vulcanization of rubber with nitro compounds.** *Ibid* 740–4.—Rubber was vulcanized with *m*-$C_6H_4(NO_2)_2$ (I) and PbO and with 1,3,5-$C_6H_3(NO_2)_3$ (II) and PbO and the course and the kinetics of the reaction were studied by detg. the combined N at progressive stages. For these N detns. the Kjeldahl method was found satisfactory, after the uncombined I or II had been removed by extn. with acetone. The analyses and also changes in d. show conclusively that vulcanization with I or II involves a chem. reaction, and a study of the kinetics shows that in each case it is a 1st-order reaction. This is contrary to preconceived ideas and it is explained by the theory that the rubber hydrocarbon (III) and I or II form a loose mol. compd., which on continued heating is converted to soft vulcanized rubber (IV), thus: III + I (or II) ⟶ III-I (or III-I), and III-I (or III-II) ⟶ IV. The 1st reaction may be relatively rapid, so that the 2nd, which would be monomol., would mask the 1st reaction. This is in accord with the exptl. data, and with the tendency of NO_2 compds. to behave in this way with other hydrocarbons. The data suggest a stoichiometric

method for detg. the mol. wt. of rubber, though lack of knowledge of the mechanism of the reaction makes a reliable value unfeasible at present. This evidence that vulcanization by NO_2 compds. involves chem. reactions is at variance with the expts. of Fisher and Gray (*C. A.* **22**, 1704), perhaps because of the weak union of the III-I and III-II compds., so that in their expts. ICl_3 displaced the NO_2 compd. **III. Kinetics of vulcanization of rubber with sulfur and selenium.** *Ibid* 744–7.—To study the kinetics of the rubber-Se reaction, it was necessary to develop a method for the *detn. of combined Se and for total Se.* The 2 procedures are given in detail. From the data obtained with a mixt. contg. rubber, Se, *p*-$ONC_6H_4NMe_2$ and ZnO, calcns. show that the reaction involved in the vulcanization is of the 1st order and is not complicated by any side reactions. The max. coeff. of vulcanization obtained with Se was approx. 5.1%, which corresponds to a S coeff. of 2.04%. Se forms only soft vulcanized rubber. The data offer a method for estg. stoichiometrically the mol. wt. of rubber or a submultiple of it. Calcns. of the hard-rubber reaction indicate that it is a 2nd-order reaction, and it does not proceed simultaneously with the formation of soft vulcanized rubber, *i. e.*, in a single mol. the soft-rubber reaction must be completed before more S reacts to form hard rubber. *En masse* both reactions proceed simultaneously. The calcns. also show that org. accelerators shorten the time of the soft-rubber reaction so that the hard-rubber reaction begins sooner, but they do not accelerate the hard-rubber reaction. **IV. A theory of vulcanization of rubber.** C. R. Boggs and J. T. Blake. *Ibid* 748–55.—The new theory aims to explain completely the various phenomena which take place in the vulcanization of rubber. It is a purely chem. theory and is based on ideas already advanced by Bog s and Follansbee (*C. A.* **21**, 1566) and by Blake (above). It is summarized in the following 11 postulates: (1) Vulcanization is a chem. reaction in which the vulcanizing agent adds to all or to part of the double bonds of the rubber mol. (2) There are 2 possible stable addn. compds. of rubber and vulcanizing agents, soft vulcanized rubber and hard vulcanized rubber. (3) There are 2 types of chem. unsatn. in the rubber mol. corresponding to these 2 addn. compds. After the soft-rubber bonds are satisfied, the addn. of S to part of the double bonds taking part in the formation of hard rubber gives rise to a 3rd and unstable substance termed intermediate or partially formed hard rubber. (4) Some vulcanizing agents form only soft vulcanized rubber, because they are incapable of adding to all the double bonds. (5) The 2 reactions take place successively in any 1 mol. during vulcanization with S. (6) Accelerators hasten the formation of soft vulcanized rubber, but have practically no effect on the rate of formation of hard rubber. The best phys. properties of soft vulcanized rubber are obtained when the formation of soft rubber is completed, and a min. of intermediate hard rubber has been formed. (7) A definite relationship between the phys. properties and the combined S exists only when intermediate hard rubber is not formed. (8) The proportion of combined S needed to produce pure soft vulcanized rubber is approx. 0.5%, which corresponds to $(C_5H_8)_{200}S_2$. (9) The normal deterioration of soft vulcanizates with age is a result of oxidation of the rubber mol. when the formation of hard rubber has begun but has not been completed. (10) During the formation of hard rubber, S is added progressively from 1 end of the mol. to the other. This gives rise to dipoles which have a max. effect when the reaction is about 0.5 completed. This is a satisfactory explanation of the elec. properties. (11) Reclaiming causes decompn. of the vulcanized rubber mol. into 2 parts, 1 contg. practically all the combined S and insol. in $CHCl_3$ and the other contg. no S and sol. in $CHCl_3$.

C. C. Davis

Aging of hot-vulcanized dipped goods by the Bierer-Davis test. Anon. *Gummi-Ztg.* **44**, 1800(1930).—Representative samples of com. dipped goods cured by the ordinary hot method with S, and others by S_2Cl_2, were aged in O (18 atm.) at 65°. Judged by the compressed-O aging test, the hot-vulcanized dipped goods were much superior to the goods cured with S_2Cl_2.

C. C. Davis

Rubber. A. Barazzetti. *Rev. gén. plastiques* **3**, 173–5, 249–50, 321–4, 453–6, 518–21, 709–13(1927); **4**, 45–9, 109–12, 173, 175, 301–5, 427–8, 489–94, 553–8, 617, 619, 681–8(1928); **5**, 45–50, 107–12, 173–9, 293–301, 419–26, 547–53, 611–20(1929).—A review dealing with the history, distribution and cultivation of rubber, phys. and chem. properties of the latex, method and theories of coagulation, compn., constitution, phys. and chem. properties and phys. and chem. tests of crude rubber, and synthesis of rubber. A large no. of references are scattered through the article.

A. P.-C.

The heat of swelling of raw rubber. Answer to the remarks of Lothar Hock. P. Stamberger and C. M. Blow. *Kolloid-Z.* **51**, 376(1930); cf. *C. A.* **24**, 3921.

Arthur Fleischer

Isoprene and rubber. XX. Colloidal nature of rubber, gutta-percha and balata. H. Staudinger. *Ber.* **63B**, 921–34(1930); cf. *C. A.* **24**, 3131.—*1. Mol. wt. of rubber,*

gutta-percha and balata.—In the preceding paper of this series the mol. wt. of rubber and balata was calcd. from the relations between the sp. viscosity, η_{sp}, and the mol. wt. on the assumption that the relationships which had been found for the hemi-colloid degradation products hold also for the eucolloids. The term sp. viscosity was used for η_{r-1}, *i. e.*, for the increase in viscosity produced by a substance at a definite concn. in a definite solvent. The const. calcd. by Duclaux, in his study of nitrocellulose solns. from the Arrhenius formula, $K = \log \eta_r/c$, for the relation between viscosity and concn., is designated in the present paper as the *viscosity-concn. const.*, K_c and the earlier const. K_m in the formula $\eta_{sp} = K_m c M$ is called the *viscosity-mol. wt. const.* It is shown elsewhere (*C. A.* **24**, 3754) for various polystyrenes that the mol. wt. of a eucolloid polystyrene can be calcd. from the formula $M = K_c \times 10^4$. The value of K_c for hemicolloid degradation products of gutta-percha and rubber, with av. mol. wts. of 2400, 3300, 4200 and 6500, has been found to be 0.31–0.34, 0.36–0.40, 0.44–0.45, 0.63–0.70, resp. Here, too, K_c is approx. directly proportional to the mol. wt. and the above formula can be used to det., as a 1st approximation, the unknown mol. wts. of eucolloid rubber and balata. The following values for $M = K_c \times 10^4$ and $M = \eta_{sp}/cK_m$, resp., were obtained for various rubber prepns.: Rubber purified according to Pummerer: easily sol. fraction 56,000, 52,000; difficultly sol. fraction 77,000, 73,000. Balata from latex 51,000, 52,000. Crepe rubber, about 160,000, 180,000. Masticized rubber 30,000, 25,000. *2. Constitution of rubber, gutta-percha and balata.*—The differences between rubber on the one hand and gutta-percha and balata on the other hand are not due to differences in mol. wt., since the differences still persist in partly degraded rubber with the same av. mol. wt. as gutta-percha and in the hemicolloid degradation products. S. believes the difference is due to the gutta-percha and balata being the *cis*- and rubber the *trans*-form of the polyprene; after reduction of the double bonds the differences disappear. Rubber is assigned the *trans*-configuration because its d. is smaller than that of cryst. balata. The sym. (*cis*) mols. are more tightly packed, in soli l form, than the unsym. (*trans*) forms, and the crystallizability of balata and gutta-percha also points to a sym. structure of their mols. *3. Form of the rubber, gutta-percha and balata mols.*—The increase in sp. viscosity of hemicolloids proportionally with increase in mol. wt. can be explained only by assuming that the thread mols. in soln. are rigid, an assumption further confirmed by the ready crystallizability of balata, the appearance in the liquids of Röntgen interferences which in homologous series change uniformly with the length of the mols., and the increase in fragility of the mols. with increase in their length. *4. Nature of the colloidal solution of rubber, gutta-percha and balata.*—To the view that there is a gradual gradation from the hemicolloid polyprenes of low mol. wt. to the macromol. (eucolloid) polyprenes, all being built up on the same principle in the sense of the Kekulé structural theory, it might be objected that between the substances of high mol. wt. (rubber and balata) and the degradation products of lower mol. wt. there are differences which cannot be explained merely by differences in mol. size. Thus, rubber swells and lower polyprenes dissolve normally; with the colloid-sol. rubber the osmotic pressure increases with concn. and with the lower polyprenes it decreases; the increase in viscosity of eucolloid solns. with the concn. is extraordinary. These differences are explained, however, by the fact that the "sphere of influence" (*Wirkungsbereich*) of macromols. is much greater than that of small mols. That the sp. viscosities of solns. of polymer-homologs of equal concn. are not alike, as would be expected from the Einstein formula, but increase proportionally with the mol. wt. can be explained by assuming that the spheres of influence of the mols. are not proportional to their vol. but to the square of their length, so that in solns. of equal concn. the sphere of influence of the relatively few macromols. is far greater than that of the much more numerous hemicolloid mols. Assuming that the isoprene residue in the polyprene chain is about 4.5 A. U. long and 2 A. U. wide and that the mols. form not single but double threads, the diam. (d) of such a double mol. would be about 6 A. U. Assuming, further, that the sphere of influence is $(h/2)^2 d$ (where h is the length of the mol.), the sphere of influence of the macromols. in a 0.1 M soln. (6.8 g./l.) of rubber (mol. wt. 170,000) would be 3.6 times greater than the available vol. of liquid, in a soln. of balata (mol. wt. 48,000) it would be equal to the vol. of the soln., and in the hemicolloid solns. it would be much less than the vol. of the soln. Conversely, the sphere of influence equals the vol. of the soln. in a 0.2% soln. of rubber or a 0.68% soln. of balata while 6.8% and more of hemicolloid polyprenes can be obtained in true soln. Only very small concns. of the products of higher mol. wt. can therefore be obtained in true soln. and it is only within these ranges of concn. that the osmotic laws and the Einstein viscosity formula hold. These very dil. solns. are designated as *sol solns.*, and the more concd. ones, where the sphere of influence is greater than the vol. of the soln., as *gel solns.* The numerical values given above

are of course only approximations intended merely to represent orders of magnitude, and the views developed apply only to homeopolar mol. colloids; with heteropolar mol. colloids, like proteins, and coördinative mol. colloids (the polysaccharides) the relationships are much more complicated. C. A. R.

Spanish rubber. J. García Viana and M. Tomeo. *Anales soc. españ. fís. quím.* **28,** 709–17(1930).—A sample from the Canary Islands and from Guinea contained 27.14 and 12% rubber, resp. Data are given on d., loss of wt. on washing, viscosity, properties of the resins, entrainment by water vapor, microscopic studies of the latex and vulcanization. These samples are not important commercially. E. M. S.

Structural changes during the processing of rubber. Ernest A. Grenquist. *Ind. Eng. Chem.* **22,** 759–65(1930); cf. *C. A.* **23,** 4097; Hauser, *C. A.* **24,** 750.—The expts. deal with the effects of mastication, of heating in air, in O, in steam and in CO_2 and of light on the plasticity of raw rubber. In this way the relative effects of mech. work, atm. O and heat could be distinguished. These relative effects were judged by changes in the plasticity (measured by flow and recovery) following the particular treatment. The results, in general, show that plasticity is a function of the state of aggregation of the rubber hydrocarbon, and to a lesser extent of the degree of "breakdown," fusion or burning of the globules. Cold breakdown causes destruction of the globules and fusion of the product and disaggregation of the hydrocarbon. The softness is permanent and no other agency was found which causes such destruction of the elasticity as does prolonged cold phys. mastication. When rubber is heated in air the globules are partly destroyed and fused, with accompanying thermal disintegration and oxidation. O is necessary for the destruction and fusion at the temps. used in the expts. When rubber is heated in steam, the globules are not destroyed and the increase in plasticity is caused by thermal disaggregation of the hydrocarbon, which on standing is followed by reaggregation. At any given temp. of heating, the greatest disaggregation occurred in CO_2. These plastic changes are reversible as long as the globular structure remains intact. The phenomena were more complicated when rubber was exposed to ultra-violet radiation, for both aggregation and disaggregation seemed to occur successively. The plasticity detns. were made with an app. which was a modified form of the Williams method. The relation between elasticity and double refraction was also studied. The latter diminished progressively with increase in plasticity, *i. e.*, it was directly proportional to the recovery after flow, and when the elastic properties were destroyed anisotropy was no longer visible. C. C. Davis

Some studies relating to the compression and shear resistance of rubber. J. H. Ingmanson and A. N. Gray. *India Rubber World* **82,** No. 4, 53–6(1930).—The Hippensteel compression machine (cf. *C. A.* **22,** 2855, 4272) is, in conjunction with the compressed O aging test, a satisfactory practical method of evaluating the quality of rubber insulated wire, *i. e.*, the resistance to cutting, the centralization of the conductor and the adhesion between conductor and insulation. Various tests with different vulcanized rubber mixts. are described, including (1) the compression characteristics of 3 types of rubber-covered wire; (2) compression, shear and loose tube characteristics detd. on 17-gage conductor and $^1/_{32}$ rubber insulation; (3) the effect of aging on compression, shear and adhesion of rubber insulation; (4) the effect of O bomb aging on compression, shear, tensile strength and elongation (av. values of com. rubber-covered wires, 14-gage conductor, $^5/_{64}$ wall insulation); (5) the effect of mandrel diam. and thickness of rubber on shear load; (6) the effect of hard asphalt on tensile strength, tensile product and resistance to shear; (7) the effect of substituting reclaimed rubber for smoked sheet; (8) the effect of loading with clay on tensile strength, tensile product and resistance to shear; (9) the effect of lubrication of surface on the compression of a "pure gum" mixt.; (10) the effect of cross-sectional area of compression in the compression of a solid tire mixt. (lubricated surface); (11) compression characteristics of various materials; (12) compression characteristics of various rubber mixts.; (13) compression characteristics of pure balata and (14) compression and hysteresis characteristics of a tire tread mixt. C. C. Davis

Isoprene and rubber. XIII. The constitution of rubber. H. Staudinger, M. Asano, H. F. Bondy and R. Signer. *Rubber Chemistry and Technology* **3,** 494–510 (1930).—English version of *C. A.* **23,** 2847. **XVII. The fractionation of balata.** H. Staudinger and H. F. Bondy. *Ibid* 511–5.—English version of *C. A.* **24,** 3130. **XVIII. Viscosity studies on balata.** H. Staudinger and E. O. Leopold. *Ibid* 516–8.—English version of *C. A.* **24,** 3130. **XIX. The molecular size of rubber and balata.** H. Staudinger and H. F. Bondy. *Ibid* 519–21.—English version of *C. A.* **24,** 3131. C. C. Davis

A spiral model of rubber. H. FIKENTSCHER AND H. MARK. *Rubber Chemistry and Technology* **3**, 201–6(1930).—An English version of *C. A.* **24**, 3395. C. C. DAVIS

Industrial safety. Chemical risks in the rubber industry. R. BRIGHTMAN. *Ind. Chemist* **6**, 252–4(1930).—A review with 12 references. C. C. DAVIS

Some engineering problems in the rubber industry. H. C. YOUNG. *Rubber Chemistry and Technology* **3**, 343–9(1930).—A review and discussion with various suggestions and improvements. C. C. DAVIS

New industrial applications of rubber. T. L. GARNER. *Ind. Chemist* **6**, 227–8 (1930).—A brief review, with special reference to surfacing other materials with rubber. C. C. DAVIS

Rubber linings in the chemical industry. J. COURBIER AND TH. BOUSSAND. *Chimie & industrie* **23**, 1099–1100(1930).—A brief description of their process of manuf. and their applications, and a discussion of their merits. A. PAPINEAU-COUTURE

A new way of manufacturing rubberized materials. G. WANRKE. *Kautschuk* **6**, 141–2(1930).—Mech. features of a continuous process of vulcanization are discussed briefly. C. C. DAVIS

Tests of some fillers in industrial mixtures, with special reference to their electrical properties. F. JACOBS. *Caoutchouc & gutta-percha* **27**, 15044–6(1930).—Expts. on certain elec. properties of mats are described. C. C. DAVIS

The surface energy between rubber and fillers. FRITZ HARTNER. *Rubber Chemistry and Technology* **3**, 215–28(1930).—English version of *C. A.* **24**, 3131. C. C. D.

Chemical adsorption studies of rubber fillers and rubber compounds. G. FROMANDI. *Rubber Chemistry and Technology* **3**, 229–34(1930).—English version of *C. A.* **24**, 3395. C. C. DAVIS

Sipalin as a softening agent in the rubber industry. E. WURM. *Kautschuk* **6**, 51–2(1930); cf. Ditmar and Preusse, *C. A.* **24**, 1247, 2915.—Sipalin AOM (methylcyclohexyl adipate) is an excellent softener for rubber mixts., since it minimizes the tendency of mixts. to become overheated during mixing and milling and reduces the length of time of mastication and mixing. C. C. DAVIS

The berginization of raw rubber. H. I. WATERMAN, R. H. DEWALD AND A. J. TULLENERS. *Rubber Chemistry and Technology* **3**, 33–4(1930).—English version of *C. A.* **23**, 5349–50. C. C. DAVIS

Structural differences in masticated and unmasticated raw rubber mixtures and vulcanizates, and their significance from a practical point of view. E. A. HAUSER WITH M. HÜNEMORDER. *Rubber Chemistry and Technology* **3**, 35–7(1930).—English version of *C. A.* **24**, 750. C. C. DAVIS

Quebrachitol from the serum of Hevea latex. T. G. LEVI. *Rubber Chemistry and Technology* **3**, 1–2(1930).—English version of *C. A.* **24**, 524. C. C. DAVIS

The coagulation of Hevea latex. N. BEUMÉE-NIEUWLAND. *Rubber Chemistry and Technology* **3**, 353–60(1930).—English version of *C. A.* **24**, 523. C. C. DAVIS

The natural coagulation of Hevea latex. ALEXANDER S. CORBET. *Rubber Chemistry and Technology* **3**, 254–63(1930).—See *C. A.* **24**, 1761. C. C. DAVIS

Measurements of the p_H value of rubber latex. J. G. MACKAY. *India Rubber J.* **79**, 353(1930).—Hauser has proved that the best method for detg. the H-ion concn. of latex is with a Wulff p_H app., so measurements were made to det. the precision and usefulness of this instrument. Standard solns. with p_H values of 4.0–12.0 were prepd. and 5 groups were chosen for sep. study, *viz.*: 2.6–5.0, 5.0–7.2, 7.0–9.0, 8.2–10.8 and 10.1–12.6, resp. *1st Group.*—Only the 4.0–5.0 range could be studied. Within this range the app. is precise at 4.0–4.4, while values of 4.6–5.0 are difficult to distinguish. *2nd Group.*—The app. is precise only at 5.8–7.2, for at 5.0–5.6 the shades are not distinct. *3rd Group.*—The app. is precise only at 8.0–9.0. *4th Group.*—The app. is precise at 8.6–10.8. *5th Group.*—Only the range 10.1–12.0 could be studied, and within this the app. is precise at 10.6–12.0. In this range the work must be carried out quickly, for absorption of CO_2 is rapid. Since latex coagulates at 6.0 the app. should be useful with preserved latex, and the only disadvantage is the break in continuity between 7.2 and 8.0. This can be overcome by using a series of standard p_H solns. in conjunction with the app. C. C. DAVIS

The swelling of latex. F. EVERS. *Rubber Chemistry and Technology* **3**, 361–9 (1930).—English version of *Kautschuk* **6**, 46(1930). C. C. DAVIS

The swelling of rubber latex. F. EVERS. *Kautschuk* **6**, 46–50(1930); *Rubber Chemistry and Technology* **3**, 361–9 (1930)(in English).—The expts. deal with various swelling phenomena observed when latex is in contact with solvents such as C_6H_6, toluene, etc. When latex (preserved with NH_3) was dild. 5-fold and shaken with an equal vol. of C_6H_6, a stiff jelly was obtained, which indicates that C_6H_6 may act as a coagulant instead of a solvent. When benzene was superposed on dil. latex contg.

NH_3 and allowed to stand at 20°, a swollen middle stratum was found, and the higher the NH_3 content the thicker was this stratum. Simultaneous with the swelling, the C_6H_6 became turbid, and the higher the % NH_3 the greater the turbidity. The turbid C_6H_6 was optically empty, so it is unlikely that the turbidity is caused by protein. Moreover, there was no sedimentation, and the turbidity may represent water. With much more dil. latex and with different concns. of NH_3, the phenomena (creaming only when both were dil.) indicated that high concns. of NH_3 protect the latex particle by forming a layer impenetrable to C_6H_6. When this protection is lacking, the C_6H_6 diffuses into the individual particles and brings about a gradual swelling. This is, however, contrary to earlier swelling expts. There is a distinction between the swelling of latex particles and of the coherent layer of previously individual particles, and swelling of latex takes place only to such an extent that there is an accumulation of particles in the boundary layer, with subsequent coagulation. The formation of absorption layers at the boundary surface was observed by a Péterfi micromanipulator. In contact with solvent, the latex particles contracted until only shriveled membranes remained, and in the boundary layer there was absorption of a substance in the form of a membrane. Solvent could diffuse through this, whereas no water passed into the micelle. The latex particles in the vicinity were not destroyed by the drops of solvent. By a special *technic* which is described, it was also possible to aggregate latex particles in the boundary layer between solvent and serum. In general the expts. show that the swelling of latex by org. solvents is governed by (1) the NH_3 content of the latex, and (2) the formation of a boundary layer at the surface of contact of the 2 liquids. Latex rich in NH_3 on contact with aromatic hydrocarbons forms a boundary layer which swells in turn, with a great increase in volume. Latex poor in NH_3 forms no boundary layer and therefore does not swell. On the other hand, the hydrocarbon may diffuse into the latex without disturbing the Brownian movement. Subsequently the diffused hydrocarbon is able to swell the individual latex particles. Under some circumstances it is advantageous to use latex with a high NH_3 content. If a fabric is to be impregnated with latex, it is best to use latex with a high NH_3 content, since it forms a thick boundary layer. This will then adhere firmly to all solid boundary surfaces, so that the impregnation is better than by evapn. C. C. DAVIS

The swelling of rubber. P. STAMBERGER AND C. M. BLOW. *Rubber Chemistry and Technology* **2**, 591(1929).—See *C. A.* **23**, 4846. C. C. DAVIS

Effect of pigmentation on the work of retraction of rubber compounds. F. S. CONOVER. *Ind. Eng. Chem.* **22**, 871–4(1930).—Comparative phys. tests of vulcanizates made from a base mixt. with different pigments in different proportions show that the particular pigment and its proportion have far less influence (almost none) on the work of retraction from any elongation than they do on the work of extension. The stiffer the stress-strain curve on extension the lower is the retraction curve, and the retraction curves of 2 vulcanizates which differ only in the kind and proportion of pigment cross in returning from the same elongation. The work of retraction depends to a certain extent upon the state of cure of vulcanizates, increasing with the time of cure when measured from elongation below rupture, and reaching a max. and then decreasing when calcd. from the elongation at rupture. The pigments included gas black, clay, barytes and 2 types of ZnO. C. C. DAVIS

Color reactions of rubber and gutta-percha. F. KIRCHHOF. *Rubber Chemistry and Technology* **3**, 32–3(1930).—English version of *C. A.* **24**, 749. C. C. DAVIS

Organic coloring agents in the rubber industry. F. JACOBS. *Caoutchouc & gutta-percha* **27**, 15042–4(1930).—A preliminary note. The technic employed in testing various org. colors, the results of which are to be published later, is described. C. C. DAVIS

Influence of light on the color of white rubber. W. J. S. NAUNTON. *India Rubber J.* **80**, 774(1930).—Expts. described by Rimpel and Hermann (*C. A.* **23**, 4370) were repeated with ultra-violet light instead of sunlight, and with mercaptobenzothiazole as accelerator. The results did not agree with those of R. and H., for the 1st and 3rd samples darkened and the 2nd and 4th remained unchanged. Consequently the darkening agent is S and not the accelerator. This is proved further by printing a pattern on rubber with a mask, curing for a brief time and bathing the surface with naphtha, in which case the light parts swell much more than the dark parts, giving a bas-relief effect. This suggests the prepn. of *printing blocks* by this method. Attempts to develop dark patterns, before curing, by photographic developers and powerful reducing agents, *e. g.*, alk. *p*-$HOC_6H_4NH_2$, were unsuccessful. Darkening by ultra-violet light can be obtained on rubber contg. an aldehyde aromatic amine accelerator but no S. However, this results from the action of the light on the accelerator, and bears no re-

lation to the phenomena described previously by Defries and N. (*C. A.* **23**, 2068). C. C. DAVIS

Selenium red and the new [Vulkan] blue in rubber mixtures, with and without paraffin oil, vulcanized in a press or in air. RUDOLF DITMAR AND C. H. PREUSSE. *Caoutchouc & gutta-percha* **27**, 15002–3(1930); cf. *C. A.* **23**, 5611.—Tests with the base mixt.: pale crepe 100, S 3, accelerator (6 different ones) 2, ZnO 10, $CaCO_3$ 30, color 10, with and without paraffin oil 8, show that: (1) neither Se red nor the new Vulkan blue gives any more intense colors with paraffin oil than in its absence; (2) the tones are different in all cases when vulcanized in air and in a press and (3) unsatisfactory results (undercuring, porosity and other troubles) are obtained with both Se red and the blue when the mixts. are vulcanized in hot air. C. C. DAVIS

The permeability of rubber mixings. W. CECIL DAVEY AND T. OHYA. *Rubber Chemistry and Technology* **3**, 96–8(1930).—See *C. A.* **23**, 5350. C. C. DAVIS

Studies in the oxidation of rubber mixings. W. CECIL DAVEY. *Rubber Chemistry and Technology* **2**, 571–5(1929).—See *C. A.* **23**, 4100. C. C. DAVIS

Studies in the oxidation of rubber mixings. W. CECIL DAVEY. *Trans. Inst. Rubber Industry* **5**, 386–402(1930).—The expts. are a continuation of earlier ones (cf. *C. A.* **23**, 4100) in which vulcanizates were oxidized at 70°. In the present case a temp. of 100° was used, and the effects of the oxidation are compared with those at the lower temp. With unextd. rubber-S vulcanizates, oxidation during the earlier stages was 4–5 times as rapid at 100° as at 70°. The increase of the acetone ext. to a max. and its subsequent fall was more striking at 100° than at 70°. At 100° there was less difference in effect among the various cures than at 70°. With acetone-extd. rubber-S vulcanizates oxidation was about 4 times as fast at 100° as at 70°. The formation of acetone-sol. products was at first large, but polymerization soon took place and the exts. during the period of constancy were lower than those at 70°. The ratio: acetone ext./wt. increase indicates the extent to which the absorbed O becomes acetone-sol. products. In the early stages this ratio was about the same at 100° as at 70°, but after prolonged oxidation it was much lower at 100°. Apparently at 100° oxidation was relatively rapid with respect to polymerization. In other ways the behavior of the acetone-extd. samples was similar to that of the unextd. samples. With accelerated mixts., oxidation in the early stages was 15 times as rapid at 100° as at 70°. With an antioxidant the increases in wt. were smaller, while its effect was relatively less at 100° than at 70°. On prolonged oxidation, the accelerated mixt. gained more wt. than the rubber-S mixt., which shows that an increase in wt. is not by itself a reliable criterion of the oxidation of different types of vulcanizates. In the early stages at 100°, the acetone exts. of the accelerated vulcanizate became greater than those of the rubber-S mixt., and the longer the cure the higher the ext. Similar results were obtained when the accelerated mixts. were previously extd. with acetone. The results differed somewhat with the particular accelerator used, but not in any essential way. In general these expts. showed that: (1) oxidation at 100° is very rapid, but the ultimate increases in wt. do not differ greatly from those for the same samples oxidized at 70°; (2) at 100° there is a marked evening-up of the rates of oxidation, and the effect of acetone extn. before oxidation is much less noticeable than at 70°; and (3) all acetone-ext. curves show maxima which depend upon the rapid change in the acetone exts. to an insol. form. This change is more nearly complete at 100° than at 70°, so that the exts. are lower. Various accelerators were then compared. In this case different cures were made, and the $CHCl_3$ ext., acetone ext., increase in wt. and physical properties were detd. after oxidation to various degrees. In general, as aging progressed, the wts. increased steadily, and the longer the cure the greater were these increases. The $CHCl_3$ exts. increased rapidly at first, then diminished, and the longer the cure the smaller the changes. The acetone exts. increased and in some cases diminished subsequently. The ratio: acetone ext./wt. increase diminished with the time of oxidation and with the degree of cure. This ratio indicates the tendency of an accelerator to maintain the rubber soft or allow it to become brittle. In general, by whatever criterion the tendency to oxidize was judged, com. accelerators of the aldehyde-amine type stood high and should be particularly suitable where heat is involved. Mercaptobenzothiazole was less satisfactory and rubber-S mixts. were much inferior to the accelerated ones. In further tests with C black, ZnO, clay and whiting, greater increases in wt. were obtained in each case, except with C black, than without filler under comparable conditions. The results indicated that the finer the filler the more suitable it is in vulcanizates subjected to elevated temps. ZnO gave particularly favorable results. The addn. of stearic acid to a rubber-S mixt. gave smaller increases in wt., lower acetone exts., lower acetone ext./wt. increase ratios and higher $CHCl_3$ exts., which indicates that stearic acid promotes the conversion of the acetone ext. to acetone-insol. products.

White factice diminished the increases in wt., and increased the $CHCl_3$ and acetone exts., and the tests indicated that even at long cures, factice reduces the tendency of a vulcanizate to oxidize. Expts. on the effect of various antioxidants are in progress. The results so far indicate that org. antioxidants change the $CHCl_3$ ext. to acetone ext. but do not greatly influence the conversion of the acetone-sol. substances to acetone-insol. products. C. C. DAVIS

Solubility of oxygen in rubber and its effect on rate of oxidation. IRA WILLIAMS AND ARTHUR M. NEAL. *Ind. Eng. Chem.* **22**, 874–8(1930).—A study was made of the influence of temp. and pressure upon the soly. of O in rubber, and of the influence of the concn. of O in rubber upon the aging of the latter. The technic and *app.* are described in detail, and the expts. lead to certain general conclusions. The soly. of O in rubber follows Henry's law. Oxidation of rubber proceeds at a uniform rate as long as the concn. of O remains above a certain min. In air at 70° the concn. of O in rubber is below that necessary for maintaining uniform oxidation at a max. rate. This should limit the use of air to vulcanizates of the highest quality, whose rate of oxidation is very small compared with the rate of diffusion of O. On the other hand, in O at 70° the soly. of O in rubber is slightly above that necessary for uniform oxidation, so that here thin samples of lower quality should oxidize satisfactorily. Elevated temps. produce a type of oxidation, the course of which is sensitive to high concns. of O and about which little is known, so the simultaneous use of a high temp. and a high pressure should be avoided. The data from which the conclusions are drawn were obtained with (1) acetone-extd. vulcanizates, both untreated further and treated with hydroquinol to retard oxidation, and (2) acetone-extd. pale crepe contg. Cu stearate to accelerate oxidation. C. C. DAVIS

Heats of combustion of rubber, gutta-percha and balata. T. H. MESSENGER. *Rubber Chemistry and Technology* **3**, 24–32(1930).—See *C. A.* **23**, 5350. C. C. DAVIS

Chemical reactions in rubber compounds. I. Reactions between pine tar and litharge. W. H. REECE. *Rubber Chemistry and Technology* **2**, 567–70(1929).—See *C. A.* **23**, 4100. C. C. DAVIS

A study of the vapor pressure diminution of rubber jellies. PAUL STAMBERGER. *Rubber Chemistry and Technology* **3**, 235–41(1930).—See *C. A.* **24**, 1762. C. C. D.

Cryoscopic measurements of rubber solutions and the separation of mixed phases from benzene solutions of rubber. IX. RUDOLF PUMMERER, ALBRECHT ANDRIESSEN AND WOLFGANG GÜNDEL. *Rubber Chemistry and Technology* **3**, 487–93(1930).—English version of *C. A.* **24**, 1102. C. C. DAVIS

Thermodynamics of rubber. I. Rubber as a system of two phases. L. S. ORNSTEIN, J. G. EYMERS AND J. WOUDA. *Rubber Chemistry and Technology* **3**, 397–402 (1930).—See *C. A.* **24**, 2635. C. C. DAVIS

An investigation of the viscosity of rubber solutions. C. M. BLOW. *Trans. Inst. Rubber Industry* **5**, 417–25(1930).—The expts. show that the viscosities of rubber solns. are increased by the incorporation in the rubber of a highly active filler, *e. g.*, a C black. Contrary to Staudinger (*C. A.* **23**, 4097) and Fikentscher and Mark (*C. A.* **24**, 1010), depolymerization is not involved, because the rubber shows the original viscosity if sepd. from the C black. The viscosity measurements were made in Ostwald viscometers at 25°. C_6H_6 solns. of rubber of various concns. (2.5–10%) were measured when made of freshly masticated rubber, of rubber 4 days after mastication and of rubber 30 days after mastication. The viscosities increased with increase in the content of C black and with the time of standing of the masticated undissolved mixts. A mixt. contg. 15% C black which swelled to a jelly in C_6H_6 could be liquefied by agitation (cf. Twiss, *C. A.* **19**, 1964; LeBlanc, Kröger and Kloz, *C. A.* **19**, 3398). The variation of the viscosity with the pressure was also studied, in this case with a Bingham viscometer. The results, which are given graphically, indicate that structure viscosity is very slight with overmasticated rubber, but very pronounced with C black mixts. Mastication seems to be a breaking down of the structure, as suggested by Klein and Stamberger (*C. A.* **19**, 1064). By the addn. of C black, a structure is again built up to some extent and the viscosity, elasticity and structure viscosity increase. This effect increases with time and can be reversed by renewed mastication. The formation of such a structure can be explained by an orientation of the rubber particles on the C black particles (cf. McBain and Davies, *C. A.* **21**, 3510). The fact that the process is slow supports this theory. Therefore, there is no relation between the viscosity of rubber solns. and the mol. wts. of the rubber, and mastication is not a depolymerization, as suggested by several investigators. Also in substantially the same form in *Kautschuk* **6**, 126–9(1930). C. C. DAVIS

Colloid-chemical changes in rubber and fatty oils. LÁSZLÓ AUER. *Rubber Chemistry and Technology* **2**, 576–90(1929).—See *C. A.* **23**, 4370. C. C. DAVIS

Solidification of fat oils by the silent electric discharge ("Voltol factice"). LOTHAR HOCK. *Kautschuk* **6**, 142–3(1930).—A preliminary report. X-ray examn. of products obtained by the action of the silent elec. discharge on various oils (cf. *C. A.* **17**, 2198; **20**, 2095) did not give any indications of a fiber structure, which might be predicted from analogy with rubber. It had been found in the previous work that these "Voltol" factices evolve gas and become sticky when heated, but in new expts. similar factices prepd. from rape-seed oil and from linseed oil were, after extn. with petr. ether, very stable when heated. With linseed oil, the prepn. was also carried out in an atm. of dil. H_2S. The product was darker brown, had an unpleasant odor, and no advantage was found in this attendant "vulcanization" by S. C. C. DAVIS

Alternating behavior of fatty acids in rubber compounds. T. L. GARNER. *Trans. Inst. Rubber Industry* **5**, 403–6(1930).—The results obtained by Smith and Boone (*C. A.* **21**, 1903) suggested expts. to det. the effect of the fatty acids already present in the rubber on the alternating effect of added acids. To this end pale crepes with high and with low acetone exts. (4.35 and 1.82%, resp.) and acetone-extd. crepe were cured for 80 min. at 300°F. in the mixt. rubber 100, S-10, ZnO-5, with and without the addn. of $^1/_{15}$ mol. of fatty acid, and the tensile strengths of the vulcanizates were measured. The results, which are presented graphically, show that the alternating effect depends upon the nature and upon the proportion of acid already present in the rubber. It is possible to mask completely the effect of added acids by using a rubber contg. a high % of fatty acids. *The effect of fatty acids on the viscosity of rubber solns.* was then detd. by adding 0.0025 mol. of various fatty acids to a 5% soln. of acetone-extd. pale crepe in CS_2 (Ostwald viscometer at 20°). All acids reduced the viscosity, but there was no alternating effect. There was no alternating effect in the ash content of rubber mixts. to which equimol. quantities of fatty acids had been added. C. C. DAVIS

The solvation of high molecular substances, especially rubber. P. STAMBERGER AND C. M. BLOW. *Rubber Chemistry and Technology* **3**, 409–17(1930).—English version of *C. A.* **24**, 2637. C. C. DAVIS

Atmospheric water cooling of rubber mills. HUGH R. LAMBERTH. *Rubber Age* (N. Y.) **27**, 425–6(1930). C. C. DAVIS

Notes on defects in smoked sheet and crepe rubber. R. G. FULLERTON. *Rubber Chemistry and Technology* **3**, 264–70(1930).—See *C. A.* **24**, 1543. C. C. DAVIS

Smoke production for the rubber industry. D. F. TWISS. *Trans. Inst. Rubber Industry* **5**, 407–16(1930).—A review and discussion of the history, properties and uses of various blacks. A general discussion follows the paper. C. C. DAVIS

Some properties of carbon black. D. PARKINSON. *Rubber Chemistry and Technology* **3**, 418–30(1930).—See *C. A.* **24**, 2636. C. C. DAVIS

Testing of carbon blacks for rubber. T. L. GARNER. *India Rubber J.* **79**, 888; *Chem. Age* (London) **22**, 536(1930). C. C. DAVIS

The aging of rubber compounded with china clay. T. J. DRAKELEY AND P. G. PACKMAN. *Trans. Inst. Rubber Industry* **5**, 426–41(1930).—The expts. are supplementary to tests of the reënforcing action of clays (cf. D. and Pollett, *C. A.* **23**, 3595). To the base mixt., pale crepe 100, S 4, diphenylguanidine 1, ZnO 5, were added various proportions of different clays with and without antioxidants ("Nonox" and "Agerite"). The vulcanizates were aged in air at 75°, up to 400 hrs. On aging, the stress-strain curves were displaced first toward the stress axis but later in the opposite direction. In general the greater the % clay the greater these displacements. With antioxidants, the displacements were smaller and the reversion began later. The higher the % clay the slower the decrease in tensile product but the effect of the quantity of clay became disproportionately less with heavier loadings. In general the rigidity diminished as aging progressed, and the greater the proportion of clay the more pronounced was this effect. Antioxidants diminished the changes in rigidity. There were no marked differences in the behavior of the individual clays. C. C. DAVIS

The aging of cotton contained in rubber goods. GUY BARR. *Rubber Chemistry and Technology* **3**, 53–61(1930).—See *C. A.* **23**, 5350. C. C. DAVIS

The manufacture of hard rubber articles. THOS. W. FAZAKERLEY. *Caoutchouc & gutta-percha* **27**, 15052–3(1930).—A review and discussion. C. C. DAVIS

Experiments on the causes of the deterioration of ebonite when exposed to light and air. D. M. WEBSTER AND B. D. PORRITT. *India Rubber J.* **79**, 239–43(1930).—The expts. are a continuation of earlier ones (cf. Fry and Porritt, *C. A.* **23**, 5613) and attempt to correlate the evolution of H_2S with the formation of a surface layer of high cond., and to det. the source of the H_2S. Three different types of hard rubber were heated at different temps. (180–250°) in H, and the rate of evolution of H_2S was detd. The results of the expts., which are described in detail with the data in tables and graphs, lead to certain general conclusions. At any given temp., the rate of evolution of H_2S

is rapid at first, then diminishes quickly, and finally remains uniform over a long period. Under given conditions, the rate of evolution of H_2S increases with increase in temp. During the heating, the hard rubber changed to a reddish color, and it became unsatd. (judged by Br absorption) and increasingly sol. in acetone and in CS_2. The decompn. resulting from such heating at temps. not above 250° does not give rise in appreciable quantities of free S or of volatile org. compds. On exposure to light to a moist atm. for 4 weeks, a surface film was formed on hard rubber which contained traces of SO_2 and H_2SO_4. These acids apparently originated from the oxidation of H_2S which was formed by decompn. of the hydrocarbon-S nucleus. In general the results indicate that when hard rubber is heated in an inert gas, S is eliminated by the splitting off of H_2S, with resultant formation of unsatd. substances. This is not necessarily what happens in normal aging at room temp., for simultaneous oxidation probably takes place, with formation of products corresponding to those from soft vulcanizates. To what extent these oxidation products affect the dielec. properties is unknown, but probably only to a slight extent as far as surface leakage is concerned, for the latter probably depends upon surface moisture contg. electrolytes. Expts. show that these electrolytes are derived not only from free S but also from decompn. of basic substances, and accordingly the problem of the elec. deterioration of hard rubber is related to the chem. stability of the hard rubber, so that elec. deterioration will be minimized by an increase in the chem. stability. C. C. DAVIS

Manufacture of ebonite dust moldings. I. A review of the conception and progress of ebonite dust molding. FRANK A. BATH. *India Rubber J.* **79**, 925–6; **80**, 67–8 (1930). C. C. DAVIS

Condensation products of aminophenols with aldehydes. T. G. LEVI. *Rubber Chemistry and Technology* **3**, 51–2(1930).—An English version of *C. A.* **24**, 351. C. C. DAVIS

The manufacture of insulating tape. PETER WERNER. *Gummi-Ztg.* **44**, 1602 (1930).—In English in *India Rubber J.* **79**, 709–10(1930).—Descriptive, with diagrams. C. C. DAVIS

World trade in reclaimed rubber. H. W. NEWMAN. *Commerce Repts.* No. **24**, 680–3(1930). E. I. S.

3-Methyl-1,3-pentadiene. HARRY L. FISHER AND F. D. CHITTENDEN. *Ind. Eng. Chem.* **22**, 869–71(1930).—In view of a suggestion by Harries (*Untersuchungen über die natürlichen und künstlichen Kautschukarten* **1919**, 250; cf. *C. A.* **14**, 1908), the attempt was made to prep. a simple homolog of butadiene and to polymerize it to a rubber. A new set of reactions was developed, whereby MeEtCO and AcH are converted to AcMeCHCH(OH)Me (I); I is catalytically hydrogenated to the corresponding glycol, *viz.*, $MeCH[CH(OH)Me]_2$ (II) and II is dehydrated to $MeCH:CMeCH:CH_2$ (III). No 1,2-diene is formed. III was then polymerized by 3 methods: (1) heating in air; (2) letting stand with Na at room temp. and (3) heating with Br peroxide (IV). Soft, tacky, rubber-like products were obtained by long heating in air and in the presence of IV, while oily, sticky polymers were obtained by heating, or by long standing at room temp. with Na. The yields varied from 16 to 52% of the total wt. On exposure to air, all the products oxidized slowly to resinous substances. The expts. show that III can be prepd. in a pure state without difficulty. However, unlike $CH_2:CHCH:CH_2$, $CH_2:CMeCH:CH_2$, $MeCH:CHCH:CH_2$ and $CH_2:CMeCMe:CH_2$, III does not polymerize to an elastic, resilient solid, and therefore polymerization of 1,3-dienes to rubber-like products does not depend solely upon the presence of a vinyl group. Prepd. by the method of Kyriakides (*C. A.* **8**, 1577) the yield of I was 10–2%, and it b. 66–8°. The yield of II by the method of Voorhees and Adams (*C. A.* **16**, 2500) was 63% and it b_{10} 103–5°. III prepd. by dehydration with $PhNH_3Br$ and HBr gave a 42% yield, and it b. 77–8°, with n_D^{21} 1.4561. C. C. DAVIS

An attempt at a rational classification of the principal accelerators of vulcanization. II. A study of the time required for vulcanization giving the maximum physical properties at different temperatures. R. THIOLLET AND G. MARTIN. *Rubber Chemistry and Technology* **3**, 38–50(1930).—English version of *C. A.* **24**, 1248. C. C. DAVIS

The influence of the principal accelerators of vulcanization on the preservation of rubber. R. THIOLLET AND G. MARTIN. *Rubber Chemistry and Technology* **3**, 207–14 (1930).—An English version of *C. A.* **24**, 3397. C. C. DAVIS

Action of selenium red on the principal accelerators. R. DITMAR. *Caoutchouc & gutta-percha* **27**, 15049–50(1930); cf. *C. A.* **23**, 3596.—Twenty-one different com. accelerators were tested with Se red by curing at 115° in the mixt.; crepe 100, S 3, accelerator 2, ZnO 10, $CaCO_3$ 40, with and without Se red 8 parts. The results in general show that Se red is superior to HgS or golden Sb as a red pigment, though with a few accelerators it has a hardening effect like Se. C. C. DAVIS

The correct calculation of the specific weight of rubber vulcanization agents. WERNER ESCH. *Chem.-Tech. Rundschau* **45**, 641–2(1930). J. PINCHACK

Conditions affecting the vulcanization of rubber. I. Heating curves of raw rubber. Y. TOYABE AND K. FUKUNAGA. *J. Soc. Chem. Ind., Japan* **32**, Suppl. binding 341–2(1929); cf. *C. A.* **24**, 2326.—When sheeted masticated rubber is heated in air, CO or H considerable evolution of heat occurs; in N little, if any, heat generation is induced. **II. Special properties of vulcanization accelerators.** Y. TOYABE, K. FUKUNAGA AND D. FUKUDA. *Ibid* 343–4.—In testing mixts. of rubber with ZnO, S and a vulcanization accelerator as to the degree of tendency to premature vulcanization ("scorching"), a softening effect is found to precede incipient vulcanization. On progressive vulcanization the $CHCl_3$ ext. increases more rapidly for accelerated mixings (contg. diphenylguanidine or $(CH_2)_6N_4$) than for the corresponding unaccelerated mixings. B. C. A.

Conditions affecting the vulcanization of rubber. III. Some properties of rubber against solvents. YUTAKA TOYABE AND KENJI FUKUNAGA. *Rubber Chemistry and Technology* **3**, 242–4(1930).—See *C. A.* **24**, 2326. **IV. Heat reaction during vulcanization.** YUTAKA TOYABE. *Ibid* 384–5.—See *C. A.* **24**, 3397. C. C. DAVIS

Aging of vulcanized rubber. VIII. Action of sunlight filtered through colored glasses on the mechanical properties of vulcanized rubber. T. YAMAZAKI. *J. Soc. Chem. Ind., Japan* **32**, Suppl. binding 367–8(1929).—Exposure of a vulcanized mixt. of fine Para rubber ($92^1/_2\%$) and S ($7^1/_2\%$) to the filtered sunlight showed that the effect of wave lengths greater than 3300 A. U. was serious, but that those greater than 4360 A. U. were less effective. **IX. Oxidation of acetone-extracted vulcanized rubber, and the behavior of the combined sulfur therein.** T. YAMAZAKI AND K. OKUYAMA. *Ibid* 368–70.—A mixt. of rubber and S was successively vulcanized, powdered, extd. with acetone and then heated for prolonged periods at 70°. The oxidized samples were found to yield sol. S compds., derived from the combined S, on extn. with acetone; these sol. S compds. contained some H_2SO_4, and the proportion of both was higher the greater the degree of vulcanization of the original sample. Although the behavior of a mixt. contg. also ZnO and diphenylguanidine was similar, the degree of the change was considerably less. B. C. A.

Aging of vulcanized rubber. X. The relation between degrees of oxidation of vulcanized rubber and the occurrence of the maximum state of acetone extracts. TAKEJI YAMAZAKI AND KAROKU OKUYAMA. *Rubber Chemistry and Technology* **3**, 378–83(1930).—See *C. A.* **24**, 3397. C. C. DAVIS

The swelling of vulcanized rubber in liquids. J. R. SCOTT. *Rubber Chemistry and Technology* **3**, 3–18(1930).—See *C. A.* **24**, 526. C. C. DAVIS

A note on the sun-cracking of vulcanized rubber. B. B. EVANS. *Trans. Inst. Rubber Industry* **5**, 442–50(1930); *India Rubber J.* **79**, 853–7(1930).—After a review of past work by various investigators, new expts. on the influence of fillers, methods of manuf. and conditions of exposure on sun-cracking are described. Three series of vulcanizates were tested: (1) rubber 100, S 8, filler 20% by vol., (2) same as (1) with gas black 1, and (3) rubber 100, S 4, diphenylguanidine 1, ZnO (I) 2, filler 20% by vol. The fillers were I, china clay (II) and light Mg carbonate (III). The samples were exposed while bent double upon themselves (1) in the open for 4 months; (2) behind glass for 4 months and (3) under a Hg vapor lamp for 1 week (with cooling). In series (1) and (3) II and III gave better results than I and II, which were nearly alike. Cracking was worse with gas black present (series (2)), which agrees with work by Shepard, Krall and Morris (*C. A.* **20**, 2595) but not with Tener, Smith and Holt (*C. A.* **21**, 4095). With the gas black, I gave better results than II and III. No definite explanation is evident. Cracking occurred mostly at right angles to the direction of mech. strain, whether the bend was across or along the calendered grain. There was no essential difference between the accelerated and the unaccelerated vulcanizates with regard to the rate at which cracking progressed. In general the smoother the surface the less the tendency to crack under given conditions. Outdoor exposure was worse than exposure behind glass. Cracking on exposure to ultra-violet light was different in character from that with sunlight. With ultra-violet light, cracking was worse with no filler, and with I than with II or III, both with accelerated and unaccelerated vulcanizates, and the dark-colored mixts. cracked worse than the corresponding mixts. without gas black. In general, ultra-violet light was not shown to simulate the effects of sunlight. C. C. DAVIS

Evolution of hydrogen sulfide from vulcanized rubber. EDWARD WOLESENSKY. *Rubber Chemistry and Technology* **3**, 386–96(1930).—See *C. A.* **24**, 3133. C. C. D.

The preparation of artificial gasoline from vulcanized scrap rubber. A. D. LUTTRINGER. *Caoutchouc & gutta-percha* **27**, 15012(1930).—A discussion of the Nishida patent (cf. N., *C. A.* **23**, 4332). C. C. DAVIS

Patents

Treating latex to improve adhesiveness of rubber produced, etc. EARDLEY HAZELL (to Naugatuck Chem. Co.). U. S. 1,757,632, May 6. A hypochlorite such as NaOCl is added. Addn. of $Na_2S_2O_3$ also facilitates creaming. Various treatments are described in some of which "Nekal," CH_2O, etc., are used.

Concentrating rubber latex. DUNLOP RUBBER CO., LTD., E. A. MURPHY and D. F. TWISS. Brit. 324,375, July 26, 1928. Reversible pastes (which may contain about 3% water) are obtained by adding non-coagulating hygroscopic substances, such as glycerol or other polyhydric alcs. or alkyl esters such as glycol monoethyl ether, to rubber or like dispersions and evapg. the water. The pastes may be rendered irreversible by kneading, molding, calendering, extruding or the like; or the stability of the pastes may be reduced by adding CH_2O or $CaSO_4$. Vulcanization may be effected by washing out the colloid if S and an ultra-accelerator have been added.

Quebrachitol from rubber latex serum. JOHN MCGAVACK and GEORGE B. BINMORE (to Naugatuck Chemical Co.). U. S. 1,758,616, May 13. Waste rubber latex serum is rendered more readily extractable by removal of water (suitably by spray desiccation) and is then treated with a hot alc. solvent which is miscible with water in all proportions, and quebrachitol is recovered from the solvent by changing the soln. ratio of the quebrachitol to the solvent (suitably by concg., followed by cooling and crystn.).

Rubber compositions. HAROLD A. MORTON. Fr. 677,605, June 28, 1929. See Brit. 314,756 (*C. A.* **24**, 1546).

Rubber composition. NORRIS GOODWIN (to Delano Land Co.). U. S. 1,758,151, May 13. A compn. which is suitable for tires, etc., comprises a rubber stock in which is incorporated a finely divided C having an oil absorption no. less than that of common com. C (and which may be obtained as described in U. S. pat. 1,758,152) and which has at least as great a stiffness as a rubber compn. contg. an approx. equal quantity of common com. C.

Treating rubber dispersions. DEWEY & ALMY CHEMICAL CO. and D. M. STEVENS. Brit. 324,287, March 19, 1929. Natural or artificial rubber dispersions are cured, without use of S, by treatment with an "active-oxygen agent" such as *m*-dinitrobenzene, *sym*-trinitrobenzene, $KMnO_4$ or benzoyl peroxide, and when desired the reaction is interrupted by the addn. of a reducing agent, such as iron filings or Al powder. In using nitro compds. with latex, a colloidal protective agent is added to prevent premature coagulation. Numerous details and examples are given.

Rubber articles from dispersions. DUNLOP RUBBER CO., LTD., D. F. TWISS, F. T. PURKIS and E. A. MURPHY. Brit. 324,104, Oct. 18, 1928. Rubber articles are made from concd. aq. dispersions by adding one or more non-coagulants for rubber, which decompose or interact to form coagulants on rise of temp., followed by heating to produce a gel. $(NH_4)_2S_2O_8$ may be used alone or with trioxymethylene, aldehydes or other neutral org. substances capable of being oxidized to acid substances, as may also $(NH_4)_2S_2O_3$ or NH_4 salts of other S-contg. acids which, by oxidation, yield compds. of greater acidity. Oxidizing agents such as persalts or H_2O_2 may be employed as may also salts, such as Pb acetate, which accelerate decompn. of the thiosulfate.

Curing rubber articles with hot circulating gases. HENRY R. MINOR (to Liquid Carbonic Corp.). U. S. 1,757,053, May 6. A curing gas such as CO_2, N or flue gas is supplied under uniform pressure; the heated gas is then caused to be recirculated to the rubber to supply addnl. heat to it, and the recirculation is accelerated by causing a pressure difference to be set up in the circulating system. An app. is described. Cf. *C. A.* **24**, 1766.

Rubber products. WILLOUGHBY S. SMITH, HENRY J. GARNETT, JOHN N. DEAN, BERNARD J. HABGOOD and HENRY C. CHANNON. Fr. 677,803, July 3, 1929. Rubber is made more suitable for elec. insulators by submitting it in the presence of glycerol to a hydrolysis with superheated water and steam sufficiently long to render sol. in water the insol. substances. The rubber may first be swollen by treatment with an org. solvent such as C_6H_6.

Rubber threads. F. C. JONES. Brit. 324,186, Dec. 13, 1928. Fine threads are formed by passing rubber through a die into a hot aq. soln. of an alk. polysulfide and thence into a drying chamber. The threads may also be passed through a soap soln. and may contain accelerators, fillers, etc.

Rubber coated fabrics. J. MANDLEBERG & CO. LTD., and J. LLOYD. Brit. 324,211, Jan. 4, 1929. Various details are described of a process which may involve embossing, decorating with a colored rubber mixt., vulcanizing, etc.

Acid- and alkali-resistant coating on metals. FRITZ AHRENS (one-half to Harzer Achsenwerke, G. m. b. H.). U. S. 1,758,420, May 13. A metal such as iron is first

coated with a soln. of rubber contg. a reaction product produced by sulfurizing oxidizable oils by use of S_2Cl_2. A coating of rubber is then applied, and vulcanization is effected.

Colored rubber goods. DUNLOP RUBBER CO., LTD., and G. W. TROBRIDGE. Brit. 324,006, Oct. 11, 1928. A mold or former is provided with a coating of an aq. dispersion of rubber of one color and there is then applied another coating of another color, followed by drying and vulcanizing. Various details of compns. and procedure are given.

"Jazz pattern" ornamentation with rubber, etc. DUNLOP RUBBER CO., LTD., E. A. MURPHY and A. NIVEN. Brit. 323,755, Oct. 6, 1928. One or more colored aq. dispersions of rubber or like material are floated onto the surface of a bath of a dispersion of different color and a former is dipped into the bath to form an article having a "jazz pattern" on the surface next to the former. Various details of compns. and procedure are described.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 323,721, Oct. 3, 1928. Diolefins such as isoprene or butadiene are polymerized in aq. emulsions (as by the use of H_2O_2 with an aq. emulsion of isoprene with olein, NH_3 and glue) and the polymerization products obtained are treated with reducing agents such as $NaHSO_3$, Na hydrosulfite, Na formaldehyde sulfoxylate, $SnCl_2$, hydroxylamine, hydrazine or its salts, phenols, naphthols, sols of metals or metal oxides, aniline, peroxydases and H, with catalysts.

Synthetic rubber. I. G. FARBENIND. A.-G. Brit. 324,004, Aug. 14, 1928. Polymerization of diolefins such as butadiene is effected with the addn. of a diluent nonreactive hydrocarbon such as cyclohexane, petroleum ether, benzene, butylene or amylene and by use of Na or other suitable polymerizing agents. The inert added hydrocarbon is preferably of such low b. p. as to be readily removed from the product by distn.

Artificial compositions resembling rubber. WALTER FRANKENBURGER and CHRISTIAN STEIGERWALD (to I. G. Farbenind. A.-G.). U. S. 1,756,943, May 6. A deriv. of vinyl alc. such as vinyl acetate is polymerized in the presence of a protein material such as casein or albumin to form a product which is capable of being stretched and thereafter resuming its original shape.

Mold for rubber tires. LAURITS A. LAURSEN (one-fourth to Pearl L. Laursen). U. S. 1,757,376, May 6. Structural features.

Steam-jacketed mold for vulcanizing tires. L. L. J. POBLIN. Brit. 323,798, Oct. 10, 1928. Structural features.

Thermostatic control for vulcanizing apparatus. FIRESTONE TIRE & RUBBER CO. Brit. 324,317, Sept. 21, 1928. Structural features.

Rubber vulcanization accelerators. JAN TEPPEMA (to Goodyear Tire & Rubber Co.). U. S. 1,757,930, May 6. Accelerators are formed by the reaction of 6-nitro-2-chlorobenzothiazole and Na diethyldithiocarbamate or of other 2-halogen benzothiazoles and dithiocarbamates. Several examples and various details are given. Cf. *C. A.* **24**, 3135.

Apparatus for vulcanizing articles such as rubber tires or casings. WALTER J. JARRATT and FRANK E. HARTMAN. U. S. 1,757,635, May 6. Structural features.

Apparatus for vulcanizing rubber sheets, strips, etc. DUNLOP RUBBER CO., LTD., H. WILLSHAW and W. G. GORHAM. Brit. 324,203, Jan. 1, 1929. Structural features.

Cold vulcanization of rubber. F. W. FARR. Brit. 324, 545, Feb. 13, 1929. Articles, such as those of rubber, of substantial thickness are uniformly vulcanized by use of a dil. soln. of S chloride and provision of channels in the mass for the distribution of the vulcanizing fluid. The channels may be formed either by loosely packing small granules or rubber (which may be coated with ZnO) or by incorporating hollow fibers in the rubber, or (in the case of sheets) by providing the material with perforations. Pressure is utilized to facilitate penetration and consolidation.

Rubber vulcanization. I. G. FARBENIND. A.-G. Brit. 324,489, Dec. 27, 1928. Polymerization products of diolefins such as those from butadiene are vulcanized in the presence of accelerators such as α-naphthylamine or piperidyldithiocarbamic acid, with a small quantity of Se or Se and S (suitably by heating with steam). Cf. *C. A.* **24**, 2640.

Vulcanizing rubber. LORIN B. SEBRELL (to Goodyear Tire & Rubber Co.). U. S. 1,757,944, May 6. Vulcanization accelerators are used comprising a reaction product of hydroquinone with isoamylamine, xylidine, dibenzylamine, dipropylamine, tributylamine or bis-amylamine. U. S. 1,757,945 relates to the production of a vulcanization accelerator by refluxing a mercaptothiazole and a Schiff base for approx. 2 hrs., *e. g.*, the accelerator may be formed by refluxing mercaptobenzothiazole with ethylidene aniline. Cf. *C. A.* **24**, 2918.

Rubber. DOROTHY M. STEVENS and ERNST A. HAUSER (to Dewey and Almy Chemical Co.). Can. 300,374, May 20, 1930. Rubber is cured by treating latex dispersed in water with an aromatic nitro compd. sol. in alk. aq. media; *e. g.*, to a 35%

natural latex add a previously prepd. pasty mixt. of 3 parts *m*-dinitrobenzene and 10 parts of a 10% aq. soln. of casein, for each 100 parts rubber in the latex. Heat to 95° and maintain this temp. for 20 min. while stirring the mixt.

Rubber compositions. HAROLD A. MORTON. Fr. 678,369, July 12, 1929. See Brit. 315,661 (*C. A.* **24**, 1764).

Composition for wear-resisting tire treads, etc. WM. H. TEST. U. S. 1,760,922, June 3. Finely divided Ti nitride is used with a resilient org. binder such as vulcanized rubber. Other nitrides also may be used such as those of Zn and Si.

Rubber dispersions. N. V. DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ. Fr. 678,512, July 17, 1929. A dispersion of rubber or the like specially suitable for making waterproof fibrous material is obtained by kneading rubber or the like with a bituminous material and dispersing the mixt. by means of an aq. and colloidal suspension of clay or the like, preferably at an elevated temp. A vulcanizer such as rubber is added to the dispersion.

Rubber sheets or strips. ERNEST HOPKINSON and WILLIS A. GIBBONS (to General Rubber Co.). U. S. 1,759,618, May 20. Continuous deposition of rubber is effected from an aq. quickly filtering dispersion upon a moving web of filtering material and the aq. portion of the dispersion is withdrawn by filtration and the deposited rubber is detached from the web without interrupting its movement. An app. is described.

Images on rubber surfaces. JOHN P. BROCKWAY. U. S. 1,761,424, June 3. A highly polished rubber surface is treated with a bath of HCl, wiped dry, an image on a transparent material is then placed in front of the rubber surface and it is exposed to light and then developed in a bath of HNO_3 and water, each 50%.

Coating metal objects with rubber. HARZER ACHSENWERKE G. M. B. H. BORNUM AM HARZ. Fr. 678,592, July 17, 1929. Coatings of rubber which are resistant to acids or alkalies are obtained on metal by applying an intermediate layer by sprinkling the metal with a suspension of latex and S mixed with acid factice, and applying a coating of rubber in known manner which is afterward vulcanized.

Reclaiming rubber. GEORGE J. MILLER. U. S. 1,759,017, May 20. Material contg. a rubber compn. and cotton is treated with acidified $ZnCl_2$ in a closed digester to remove the cotton under the action of heat and pressure, and the remaining rubber is washed in a closed digester while subjected to heat and pressure.

Age resisters for rubber. HAROLD A. MORTON. Can. 300,918, June 10, 1930. A rubber compn. includes 1,3-diphenyl-2-propyltetrahydroglyoxaline.

Antioxidant. JAN TEPPEMA (to The Goodyear Tire and Rubber Co.). Can. 300,805, June 3, 1930. Rubber is preserved by vulcanization in the presence of a reaction product of β-naphthol and formaldehyde.

Antioxidants. ALBERT M. CLIFFORD (to The Goodyear Tire and Rubber Co.). Can. 300,807, June 3, 1930. Certain aminobenzyl alcohols are incorporated into rubber goods as antioxidants or age-retarders, *e. g.*, *p*-(α-naphthylamino)-benzyl alcohol. Cf. *C. A.* **24**, 1765.

Antioxidant for rubber. HAROLD A. MORTON. Can. 300,917, June 10, 1930. In a rubber compn. is incorporated a *N*-phenyl-substituted diaminoethane in which one or more of the ethylene hydrogen atoms may be substituted by alkyl groups.

Vulcanizing rubber. CHEM. FAB. KALK G. M. B. H. and HERMANN OEHME. Ger. 497,477, June 22, 1926. Anhyd. ZnO prepd. by heating a compd. of Zn to a temp. below the glowing temp. is added to the rubber.

Treating latex. JOHN MCGAVACK (to Naugatuck Chemical Co.). U. S. 1,762,729, June 10. Latex is treated with a small proportion of Na silicate soln. and with sufficient dil. H_3BO_3 to convert the silicate into a hydrosol of silicic acid, the material is allowed to stand until gel formation occurs, and an uncoagulated latex gel is recovered, which is suitable for use in various mfg. processes. Cf. *C. A.* **23**, 5613.

Treating rubber latex. ARTHUR BIDDLE (to United Products Corp. of America). U. S. 1,762,153, June 10. Starch which has been subjected to the action of lime and NaF is added to rubber latex and there is then added an insolubilizing agent such as CH_2O, $(CH_2)_6N_4$, $K_2Cr_2O_7$, tannin or $ZnCl_2$ to insolubilize the starch after the water has been removed from it and form a compn. which may be mixed with fillers, etc., for various uses.

Treating rubber latex. WM. B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,762,494, June 10. In prepg. dispersable rubber concentrates from rubber latex, hemoglobin is added to the latex and the mixt. is subjected to spray drying in contact with air of suitable moisture content. Cf. *C. A.* **23**, 1777.

Apparatus for extrusion or straining of rubber. FRANK C. VANDERGRIFT (to National-Erie Co.). U. S. 1,762,367-8, June 10. Structural features.

Deposition of rubber. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 679,588,

July 30, 1929. In the deposition of rubber using a rubber support for dipping into the aq. dispersion of rubber, the support of rubber is wetted with an org. liquid causing the rubber to swell and having a coagulating action on the aq. dispersion of rubber or contg. coagulating substances in soln., *e. g.*, benzene contg. 5% of AcOH in soln. Cf. *C. A.* **24**, 2329.

Electrophoretic deposition of rubber. THE ANODE RUBBER CO. Ger. 498,010, Sept. 5, 1925. See Brit. 257,885, (*C. A.* **21**, 3141).

Retarding oxidation of rubber. ALBERT M. CLIFFORD (to Goodyear Tire and Rubber Co.). U. S. 1,763,579, June 10. Prior to vulcanization, rubber is incorporated with a reaction product of a phenyl naphthylamine and an aldehyde such as CH_2O. Cf. *C. A.* **24**, 989.

Inhibiting oxidation of rubber. HAROLD W. ELLEY (to E. I. du Pont de Nemours & Co.). U. S. 1,763,293, June 10. *m*-Toluylenediamine (suitably about 0.1–2.0%) is incorporated with rubber compns., in addn. to a vulcanizing agent and an accelerator which is substantially a non-inhibitor of oxidation.

Rubber mixtures. RUNGE-WERKE A.-G. Ger. 498,237, June 19, 1927. In the prepn. of rubber mixts. contg. soot, the soot is mixed with an intermediate product, *e. g.*, a soln., obtained in the regeneration of rubber, the solvent is evapd., if necessary, and the mixt. of regenerate and soot is mixed with the rubber.

Rubber mixtures and articles. K. D. P., LTD. Fr. 679,992, Sept. 9, 1927. Mixts. of latex with substances such as lampblack are made during the const. production of fresh surfaces in the mixt. and simultaneously with the drying. Fr. 679,993 described the production of rubber articles by squirting latex, mixed or not with vulcanizing agents, powd. ebonite, etc., with heat on to a mold which may be heated.

Rubber dispersions. WM. B. PRATT (to Dispersions Process, Inc.). U. S. 1,762,194, June 10. In dispersing rubber in non-aq. substances which are non-solvents for rubber such as oils, waxes, gums or bitumens, a colloid such as neutral casein is first incorporated in a rubber mass and dispersion of the mixt. is effected in the non-solvent at temps. of 120–60° without depolymerization of the rubber.

Rubber articles from aqueous dispersions. DUNLOP RUBBER CO., LTD., E. A. MURPHY, R. G. JAMES and D. F. TWISS. Brit. 324,988, Oct. 6, 1928. Rubber articles produced from aq. dispersions by dipping, spraying, spreading or electrophoresis are given a wrinkled or grained surface by bringing the uncoagulated surface into contact with one or more liquids which effect coagulation and swelling of the rubber simultaneously or successively. A mixt. of benzene with 2.5% glacial HOAc may be used, and various other examples also are given.

Preserving rubber. THE B. F. GOODRICH CO. Fr. 680,286, Aug. 12, 1929. See Brit. 317,786 (*C. A.* **24**, 2329).

Use of tolylnaphthylamine and similar compounds to render rubber compositions age resisting. HAROLD W. ELLEY. U. S. 1,763,615, June 10.

Regenerating rubber. ALEXANDER W. MORTON. Fr. 680,491, Aug. 19, 1929. Used rubber is regenerated by grinding it up, adding S, incorporating a mixt. of products causing the rubber to swell, *e. g.*, benzine 4, CS_2 1 and CCl_4 1 part, the mixt. being used in amt. of 5% of the rubber treated. Plastifying agents are added and the mixt. is vulcanized.

Finishing rubber-coated sheeting. HERBERT W. EMERY (to Archer Rubber Co.). U. S. 1,762,165, June 10. In imparting a permanent lusterless appearance to rubber-coated sheeting, the rubber of which is compounded with S, a finely divided luster-removing material such as starch or talc is applied to the rubber surface of the sheeting, the excess of the material is washed from the surface, the sheeting is subjected to complete vulcanizing by heat and the rubber is superficially hardened (suitably by a halogenizing agent).

Apparatus for testing strength of tire fabrics, etc. ERNST EGER (to Morgan & Wright). U. S. 1,762,164, June 10. Structural features.

Liner material for use in rubber tire manufacture, etc. LORIN B. SEBRELL (to Goodyear Tire & Rubber Co.). U. S. 1,763,618, June 10. Piles of rubberized material are arranged alternately with piles of liner material treated with nitrocellulose contg. di-Bu phthalate.

Mold of the "watch case type" for rubber tires. J. JONES. Brit. 324,991, Nov. 9, 1928. Structural features.

Vulcanization accelerator. JAN TEPPEMA (to The Goodyear Tire and Rubber Co.). Can. 300,806, June 3, 1930. Substituted mercaptobenzothiazoles, particularly those contg. substitutions in the aryl ring, may be employed as accelerators. Among such compds. 5-chloromercaptobenzothiazole and 6-nitromercaptobenzothiazole are included. Mercaptoarylthiazoles having one or more H atoms in the aryl ring

replaced by heavier mols., either negative or positive, may also be made to react further with amines, either aryl or aliphatic, to produce double salts, which when incorporated into a rubber compd. very powerfully accelerate vulcanization.

Vulcanizing accelerator. JAN TEPPEMA (to the Goodyear Tire and Rubber Co.). Can. 300,808, June 3, 1930. Certain salts of S-contg. compds., *e. g.*, Na diethyldithiocarbamate or the Na salt of mercaptobenzothiazole, may be caused to react with such org. halogen sulfides as 2-benzoyl-4-nitrophenyl sulfur bromide, to produce substances having excellent properties as accelerators of the rate of vulcanization of rubber.

Rubber vulcanization. DONALD H. POWERS (to E. I. du Pont de Nemours & Co.). U. S. 1,763,325, June 10. Dibenzothiazole monosulfide is used as an accelerator as are also di-3-methylbenzothiazole monosulfide and dinaphthothiazole monosulfide. Cf. *C. A.* **24**, 266.

Rubber vulcanization. LORIN B. SEBRELL (to Goodyear Tire & Rubber Co.). U. S. 1,763,619, June 10. A reaction product of mercaptobenzothiazole with ethylidene aniline is used as an *accelerator*. Cf. *C. A.* **24**, 2918.

Rubber vulcanization. WINFIELD SCOTT (to Rubber Service Laboratories Co.). U. S. 1,762,531, June 10. There is used, as an accelerator, the reaction product of butylaldehyde and a dialkylene substitution deriv. of thiuram disulfide such as diallyl thiuram disulfide.

Coloring rubber, etc. I. G. FARBENIND. A.-G. Brit. 325,967, Jan. 30, 1929. Factice compns., which may also contain glycerol, rubber softeners, plastic or viscous antioxidants and vulcanization accelerators, are colored as described in Brit. 242,274 (*C. A.* **20**, 1330), in which large quantities of insol. coloring matter such as Cd yellow are mechanically incorporated in the material until they no longer sep. from a soln., to prep. a material suitable for coloring rubber. Cf. *C. A.* **24**, 3134.

Electrodeposition of rubber, etc. SIEMENS & HALSKE A.-G. Brit. 325,401, Nov. 10, 1928. The process described in Brit. 307,747 (*C. A.* **24**, 265) is modified by the use of a balanced a. c. of other than sinusoidal form. Various modifications are described. Cf. *C. A.* **24**, 751.

Preserving rubber dispersions. DUNLOP RUBBER CO., LTD., W. H. CHAPMAN, D. W. POUNDER, E. A. MURPHY and F. T. PURKIS. Brit. 326,210, Dec. 7, 1928. A small proportion of a salt of H_2SiF_6 (or free H_2SiF_6 if the dispersion contains NH_3), which increases the viscosity and promotes gelling (which may be further promoted by adding ZnO), is added.

Rubber compositions. F. WECKERLE. Brit. 325,312, Nov. 27, 1928. A compn. which may be dissolved in cyclohexanol and sprayed in a jet of hot air may be formed of rubber, S, ZnO, an accelerator, hydroquinone, a glucoside such as esculin or a phenol-CH_2O condensation product and a filler such as asbestos, quartz or mica. "Carbide" may be added to increase the hardness of the product.

Rubber composition for tires, etc. I. G. FARBENIND. A.-G. Brit. 326,202, Aug. 30, 1928. A compn. is described formed from butadiene (polymerized with Na) 100, carbon black 40, ZnO 5, "mineral rubber" 5, wool grease 2, S 3, aldol α-naphthylamine 1 and mercaptobenzothiazole 0.6 part.

Red hard rubber composition. HERBERT E. MALONE and RALPH W. PRYOR (to Western Elec. Co.). U. S. 1,765,597, June 24. Rubber 26.5, S 8, vermillion 49.25, cottonseed oil 1.5, lithopone 12 and India rubber yellow 2.75%.

Rubber facings on cement blocks, etc. L. P. F. F. CRESSON. Brit. 325,302, Nov. 21, 1928. The process of manuf. described in Brit. 303,400 (*C. A.* **23**, 4596) is modified by (1) adding compds. capable of combining with silicic acid (such as magnesite cement, PbO or Pb_3O_4, with or without tar or drying oil) to the facing compn. or that part of it next to the cement base, or (2) by reënforcing the cement base with iron or other suitable material with or without org. or inorg. fibers. A hard intermediate layer may be formed from vulcanized rubber latex compn. contg. free S.

Hollow articles of vulcanized rubber. WILFRIED GENTH (to I. G. Farbenind. A.-G.). U. S. 1,765,666, June 24. In the formation of articles such as hollow balls, metaldehyde is used as aerating or inflating agent (in a quantity suitably about 0.5–1.0 g. for balls of 10 cm. diam.).

Impregnating threads or cords with rubber. C. H. GRAY. Brit. 325,916, Dec. 19, 1928. Threads or cords are passed through a liquid or viscous soln. of rubber in a solvent such as naphtha and the individual filaments are then passed between a pair of rollers which may be covered with rubber and are in close contact. App. is described.

Rubber latex. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 680,884, Aug. 27, 1929. NH_3 and fixed CO_2 are expelled from latex preserved with NH_3 by blowing

through the latex aninert gas such as steam at a temp. above the decompn. temp. of $(NH_4)_2CO_3$.

Treating rubber latex. ERNEST HOPKINSON and MERWYN C. TEAGUE (to American Rubber Co.). U. S. 1,765,015, June 17. In prepg. articles such as floor tiles, etc., from latex, an uncoagulated mixt. is formed from the latex together with cellulosic material such as wood flour, a vulcanizing agent such as S, and a colloidal material such as casein, etc., and the mixt. is dried with retention of the solid constituents of the latex.

Enzymes from rubber latex, for use in making synthetic rubber. I. G. FARBENIND. A.-G. Brit. 325,831, Nov. 28, 1928. Rubber latex or milk contg. enzymes firmly bound to albuminous substances is treated with proteases adapted to alter the albuminous material by degradation without destroying the enzymes naturally present; the products may be purified by electrodialysis and the enzymic material may be isolated by selective absorption. Enzymes recovered may be used for polymerization of butadiene and its homologs. Various details of procedure are described.

Rubber vulcanization mold of the "watch case type." J. JONES. Brit. 325,206, Nov. 9, 1928.

Pentasubstituted guanidines for use as rubber vulcanization accelerators. HANS LECHER and WALDEMAR ZIESER (to I. G. Farbenind. A.-G.). U. S. 1,766,755, June 24. The prepn. and use are described of compds. such as pentamethyl-, pentaethyl- and pentabutyl-guanidines, *N,N,N',N'*-tetramethyl-*N''*-ethylguanidine, *N,N,N''*-trimethyl-*N',N'*-diethylguanidine, *N,N,N',N'*-tetrabutyl-*N''*-phenylguanidine, *N,N*-dibenzyl-*N',N',N''*-trimethylguanidine, *N,N,N''*-trimethyl-*N'*-ethyl-*N'*-cyclohexylguanidine and *N,N,N''*-trimethyl-*N',N'*-pentamethyleneguanidine.

Rubber. I. G. FARBENIND. A.-G. Fr. 682,161, Aug. 5, 1929. Natural rubber or polymerized products of butadienes are preserved against aging by adding preserving agents such as aldol-α-naphthylamine, in the dissolved or emulsified state, to natural latex or the emulsions resembling latex. Cf. *C. A.* **24**, 2915.

Spongy rubber. SOC. BELGE DU CAOUTCHOUC MOUSSE. Fr. 682,381, Sept. 27, 1929. A spongy vulcanized rubber is made by submitting a mixt. of rubber and balata without resinous or waxy materials but with materials necessary for vulcanization to a pressure of 300–600 atms., or a mixt. of rubber and gutta-percha with vulcanization materials and 5–25% of a waxy or resinous substance may be treated in the same way.

Artificial rubber. I. G. FARBENIND. A.-G. Fr. 681,896, Sept. 17, 1929. Artificial rubber is made by polymerizing by the emulsion process, with or without the addn. of other substances influencing the polymerization, diolefins such as erythrene, isoprene or dimethylbutadienes in the presence of salts of org. bases with inorg. or org. acids which are capable of forming emulsions with butadiene hydrocarbons in an aq. soln. Examples are given using (1) the HCl salt or acetate of diethylaminoethyloleamide, (2) the HCl salt of diethylaminoethoxyoleanilide (by condensing β-diethylaminoethoxyanilide with oleic acid chloride), (3) pentadecylimidazoline hydrochloride of the probable formula: $Me(CH_2)_{14}\overline{C:N.CH_2.CH_2.NH}.HCl$ (by condensing the imidomethyl ether of stearic acid with ethylenediamine). Cf. *C. A.* **24**, 2918.

Artificial rubber. I. G. FARBENIND. A.-G. Fr. 682,277, Sept. 25, 1929. Hydrocarbons of the butadiene group are polymerized with alkali metals in mixt. with indifferent substances such as metallic oxides, kieselguhr, paraffin or salts such as NaCl.

Rubber substitutes. ALEXANDER E. BLUMFELDT. Swiss 137,478, June 27, 1928. A liquid condensation product insol. in water but sol. in alc., and insol. when heated, is obtained by treating epichlorohydrin with an aq. soln. of S compds. The substance is readily vulcanized. Thus, epichlorohydrin is stirred with NaOH, NaSH or Na_2S and cooled.

Rubber articles. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 681,385, Sept. 5, 1929. Tubular articles are made by causing aq. dispersions of rubber, etc., to flow through orifices of appropriate form in contact with a liquid dehydrating and coagulating agent such as those described in Brit. 303,544, acting partly or entirely by osmosis in a continuous manner. Cf. *C. A.* **24**, 2639.

Composite rubber articles. WM. B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,768,348, June 24. Articles such as axle bumpers or solid tires are made of a composite of rubber and short lengths of cord disposed at random, the rubber used being in part old vulcanized rubber and in part new bonding rubber, and the concn. of the old rubber and cords varying throughout the body.

Factice. JEAN BAER. Swiss 137,477, June 19, 1928. See Brit. 313,917 (*C. A.* 24, 1249).

Coagulating latex, etc., on a former. DUNLOP RUBBER CO., LTD., D. F. TWISS, E. A. MURPHY and W. G. THORPE. Brit. 326,282, Jan. 5, 1929. After dipping a former in concd. latex or the like, the material on the former is coagulated by treatment with an atm. contg. a volatile coagulant or with a dil. aq. soln. of a volatile coagulant.

Molding hollow rubber articles such as football bladders. DUNLOP RUBBER CO., LTD., and G. W. TROBRIDGE. Brit. 326,291, Jan. 23, 1929. Various mech. details are described. Cores of Si-Al alloy or stainless steel may be used. Brit. 326,292 also relates to similar processes.

Mold for forming inner rubber tire tubes. ALFRED A. GLIDDEN and THOMAS M. KNOWLAND (to Hood Rubber Co.). U. S. 1,767,062, June 24. Structural features.

Rubber fiber tread stock for tires, shoe soles and heels, etc. WM. B. WESCOTT (to Rubber Latex Research Corp.). U. S. 1,767,234, June 24. A stock is formed consisting of particles of partially cured rubber and fiber constituting the main portion of the material by wt., with an interstitial latex rubber gel surrounding and uniting the particles. Cf. *C. A.* **23**, 3599.

Vulcanizing rubber. INDUSTRIAL PROCESS CORP. Fr. 681,061, Aug. 31, 1929. In raising a vessel for the vulcanizing of rubber to a desired temp. by means of an agent consisting of a mixt. of gases, one of which is hotter than the other, *e. g.*, a mixt. of CO_2 and steam, the correct pressure which the colder gas should have to give the desired temp. once mixed with the warmer gas is calcd., and the pressure of the colder gas is corrected to account for the reduction of effective vol. caused by the condensation of a portion of the warmer gas when the 2 are introduced into the vessel. Fr. 681,062 describes the heating for vulcanization of rubber using CO_2 and steam, the initial temp. of the vessel being regulated before each elevation of temp.

Vulcanization of rubber. THE ANODE SERVICE LABORATORIES CO. Fr. 682,085, Sept. 20, 1929. An accelerator for the vulcanization of rubber is obtained by condensing together an aldehydic amine and an unsatd. substituted aldehyde. The aldehydic amine may be an alkylidene, and is preferably prepd. by the reaction of an aldehyde and an amine and the aldehyde may be α-ethyl-β-propylacrolein.

Timed temperature control apparatus for rubber vulcanization. ROY W. BROWN (to Firestone Tire and Rubber Co.). U. S. 1,768,349, June 24. Mech. features.

Rubber vulcanization accelerators. S. J. PEACHEY. Brit. 326,256, Dec. 13, 1928. Non-staining accelerators are obtained by heating *p*-nitrosodimethylaniline or a homolog with a primary, secondary or tertiary aromatic amine of the benzene, naphthalene or pyridine series and S.

Apparatus for vulcanizing rubber tires, etc. JOHN L. KELLY. U. S. 1,767,682, June 24. Structural features.

Fluid-conducting tree for tire vulcanizing apparatus. WALTER E. HUMPHREY and THORNTON G. GRAHAM (to Mason Tire & Rubber Co.). U. S. 1,768,406, June 24. Structural features.

Rubber. THE NAUGATUCK CHEMICAL CO. Fr. 683,507, Oct. 18, 1929. The cracking or splitting of rubber articles is prevented by treating the rubber with an α-diketone such as dibenzoyl or phenanthraquinone and then vulcanizing. Cf. *C. A.* **24**, 1249.

Thickening latex without coagulation. SIDNEY D. SUTTON (to Veedip, Ltd.). U. S. 1,770,092, July 8. Latex contg. NH_3 is treated with ZnO in finely divided state in the proportion of about 1% by wt. to an NH_3 content in the latex of 0.75–1.00% NH_4OH.

Rubber emulsions. SAMUEL E. SHEPPARD and LEON W. EBERLIN (to American Anode, Inc.). U. S. 1,769,717, July 1. A rubber soln. is exposed to chemically active rays such as ultra-violet rays until the viscosity of the soln. is reduced, and the soln. is then emulsified in an aq. bath. The product may be prepd. with a vulcanization accelerator as a constituent. Various compns. are described.

Electrodeposition of rubber. WM. A. WILLIAMS. U. S. 1,769,659, July 1. A metallic salt such as $ZnSO_4$ is added to latex without coagulation of the latex, and the salt is subjected to electrolysis in the presence of an anode electrode of the same metal as the salt.

Rubber articles. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 682,819, Oct. 5, 1929. Rubber articles obtained from aq. dispersions by any means are given a wrinkled or grained surface by bringing the uncoagulated surface into contact with a liquid or liquids which effect coagulation and swelling of the rubber concurrently or consecutively, such as AcOH and C_6H_6, or CCl_4 or AcOBu alone. Cf. *C. A.* **24**, 4426.

Rubber articles. THE ANODE RUBBER CO. (ENGLAND), LTD. Fr. 683,518, Oct. 18, 1929. Rubber articles are made from concd. aq. dispersions of rubber or like vegeta-

ble resins, vulcanized or not and (with or without) other substances, by forming gels, by the action of heat on the dispersions in which are incorporated one or more non-coagulating substances which decompose and mutually react under raised temp. to produce one or more coagulating acids. Examples of substances are NH_4 persulfate and trioxymethylene or CH_2O, AcH, para-CH_2O or $(NH_4)_2S_2O_3$. Examples of the process are given.

Rubber tire tread composition. Ross E. Jenkinson (to Goodyear Tire & Rubber Co.). U. S. 1,769,694, July 1. The outer ply of a tire is formed of a compn. comprising approx. 43% as much carbon black as rubber, with an inner ply formed of a compn. contg. approx. 1.4 times as much ZnO as rubber.

Connecting rubber treads with other materials of shoes. Wilhelm G. Rudolph. U. S. 1,770,671, July 15. Attachment of rubber to other material such as wooden heels is effected by use of an intermediate fabric layer contg. celluloid and of celluloid cement.

Press cure mold for production of rubber-soled footwear. Henry McGhee. U. S. 1,771,803, July 29. Structural features.

Forming tennis balls of rubber containing balata and vulcanizing materials. Albert E. Penfold (to Dunlop Tire and Rubber Corp. of America). U. S. 1,771,861, July 29. Mech. features.

Rubber cement. Clarence M. Carson (to the Goodyear Tire and Rubber Co.). Can. 302,811, Aug. 5, 1930. A cement contg. hemoglobin, water, S, ZnO, diphenylguanidine. latex and CH_2O is used for securing rubber to metal.

Rubber substitutes. I. G. Farbenind. A.-G. (Wilhelm Pungs, inventor). Ger. 498,598, Oct. 23, 1924. Addn. to 405,850. The methods of 405,850 and 407,245, for producing org. products useful in industry by the oxidation of paraffins and montan wax, resp., are extended to vegetable and animal oils, resins and waxes. Thus, a mixt. of montan wax and wool oil is subjected to an air current at 160–70°, giving a yellow-brown elastic mass capable of being vulcanized and used as rubber substitute. Other examples mention train oil, wool fat, linseed oil, sun-flower oil, castor oil and carnauba wax.

Rubber substitute formed from cashew nut-shell oil and glycerol. Mortimer T. Harvey (to Harvel Corp.). U. S. 1,771,785, July 29. Glycerol and cashew nut-shell oil are heated (suitably with S) to form a product which may be used as a rubber substitute. U. S. 1,771,786 describes the heating of cashew nut-shell liquid with S to obtain a product which is of rubber-like character.

Insulating material. Archie R. Kemp (to Western Electric Co., Inc.). Can. 302,866, Aug. 5, 1930. Rubber (in the form of latex or otherwise) is treated with water at 125° or more for a time sufficient to change a substantial portion of the naturally occurring nitrogenous substances therein. The rubber is then washed and rendered electrically stable under the continued influence of water.

Vulcanizing rubber. Robert H. M. L. Binay and Louis F. Pecot. Fr. 682,521, Sept. 30, 1929. A heating compn. for vulcanizing rubber articles is composed of a mixt. of trioxymethylene with a soln. of colophany in EtOH or gum arabic or fish glue in water. A suitable vulcanizing press is described.

Vulcanizing rubber. Soc. Italiana Pirelli. Ger. 501,124, Oct. 20, 1926. Vulcanization is accelerated by adding to the mix K or Rb salts of monobasic aliphatic or fatty-aromatic carboxylic acids having a dissocn. const. greater than 1×10^{-5}. AcOK, K stearate and $C_6H_5CH_2COOK$ are mentioned, as suitable addns. A suitable mix comprises rubber 100, S 8 and AcOK 2 parts.

Vulcanizing rubber to leather. Leon B. Conant (to Standard Patent Process Corp.). U. S. 1,769,943, July 8. Leather is first dehydrated at a moderate temp., then heated to a temp. substantially the same as that of vulcanization and united and hot vulcanized to rubber. Cf. *C. A.* **22**, 2292.

Ebonite composition. Harold Gray (to B. F. Goodrich Co.). U. S. 1,769,506, July 1. A sufficient quantity of a softener is intimately incorporated in an ebonite compn. to render it readily remoldable at temps. materially lower than the remolding temp. of the ebonite itself (the softener used being free from raw gum).

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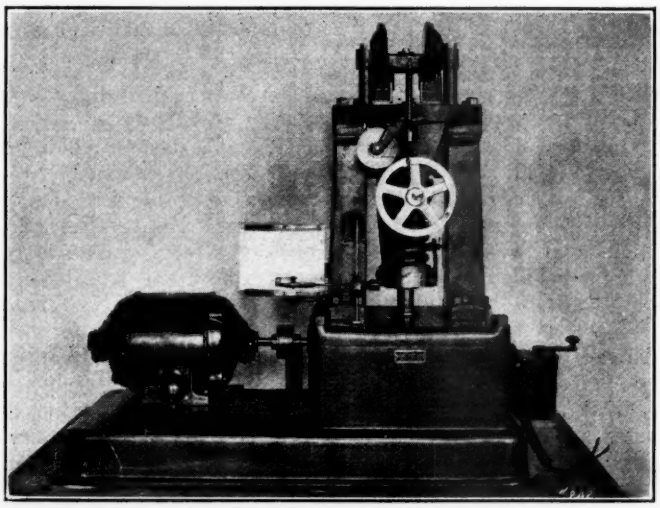
Some Studies Relating to the Compression and Shear Resistance of Rubber

J. H. Ingmanson[1] and A. N. Gray[2]

IN the past the most important method for the evaluation of vulcanized rubber has been by determination of tensile stress-strain properties. The widespread use of rubber, particularly in the automotive field, for damping vibration and absorbing shock, has created a need for a more complete knowledge of the properties of rubber under compression. As a matter of fact, rubber in use is subjected to compression and shearing to a far greater extent than to tensile stresses. Recently, a machine for deter-



Henry L. Scott Co.

Compression Rubber Testing Machine

mining the compression properties and shear resistance of rubber was described by Hippensteel.[3] This machine was designed to test rubber rapidly under compression and simultaneously to record autographically the strain under compression stress. To date it has been used primarily for the purpose

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[3] *Ind. Eng. Chem.*, 18, 409-11 (1926). *Bell Laboratories Record*, 5, 153-55 (1928).

of controlling the quality of rubber covered wire used by the Bell System. Sufficient work, however, has been completed to show that it can be used to determine the shear and compression resistance of rubber stocks in general, and it is felt that these methods may find a general application in the evaluation of vulcanized rubber.

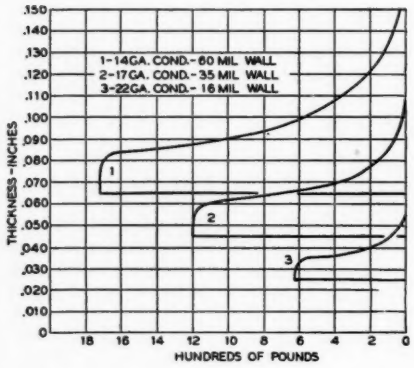

Fig. 1. Compression Characteristics of Three Types of Rubber Covered Wire

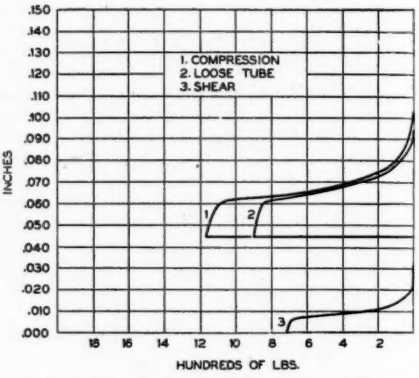

Fig. 2. Compression, Shear, and Loose Tube Characteristics as Determined on 17 Gage Conductor with 1/32 Rubber Insulation

Important requirements for a rubber insulation other than electrical are taken to be (1) resistance of the insulation to cutting by the conductor, (2) centralization of the conductor, (3) some degree of adhesion between conductor and insulation, and (4) a reasonable maintenance of these properties for a considerable period of time when the wire is exposed in service to a wide variety of climatic conditions. The compression machine and the Bierer and Davis oxygen bomb have been found to be suitable testing instruments for evaluating wire in respect to the above requirements.

The compression test as applied to rubber covered wire involves the compression of a two-inch length of insulated wire between steel blocks with parallel plane surfaces which are brought together at a rate of approximately 1½ inches per minute when not under load. The result of this treatment brings about an ultimate shear of the rubber between the conductor and one or both of the jaw faces. The occurrence of simultaneous breaks on both sides of the conductor on successive tests made on adjacent sections turned 90° from one another is taken as an indication of centralization of the conductor. Examples of the compression stress-strain relationships on several types of rubber covered wire are shown in Figure 1.

This test is applicable only in cases of solid conductors and where the wall thickness of insulation does not appreciably exceed the diameter of the conductor. In the case of stranded conductors or where wall thickness of insulation is great, the insulation may be evaluated by shear tests made on the insulation after removal from the conductor with a mandrel having a cutting edge similar to a conductor.

It has been found that the compression resistance of rubber insulation on a wire can be resolved into three main components: namely, the shear or cutting resistance of the rubber between the jaws of the machine and the con-

ductor; the actual compression resistance of the rubber on each side of the conductor between the two jaw faces; and the adhesion of the insulation to the conductor.

The shear load or resistance to cutting is determined by compressing to rupture between one jaw of the machine and a mandrel, a piece of the insulation which has been split longitudinally after removal from the conductor. The mandrel which is mounted in the head of the machine is generally selected to have a cutting edge with a radius of curvature the same as that of the conductor. The effect of sidewall compression and adhesion are entirely eliminated in this test.

The adhesion is evaluated by determining the load necessary to rupture the insulation on the wire before and after a period of immersion in mercury sufficient to amalgamate the tin coating and loosen the insulation from the conductor. The difference between the original compression load and that obtained on the loosened insulation is attributed to adhesion.

The difference between the compression load obtained on the loosened insulation and the shear load obtained on the half section with the mandrel is attributed to sidewall compression.

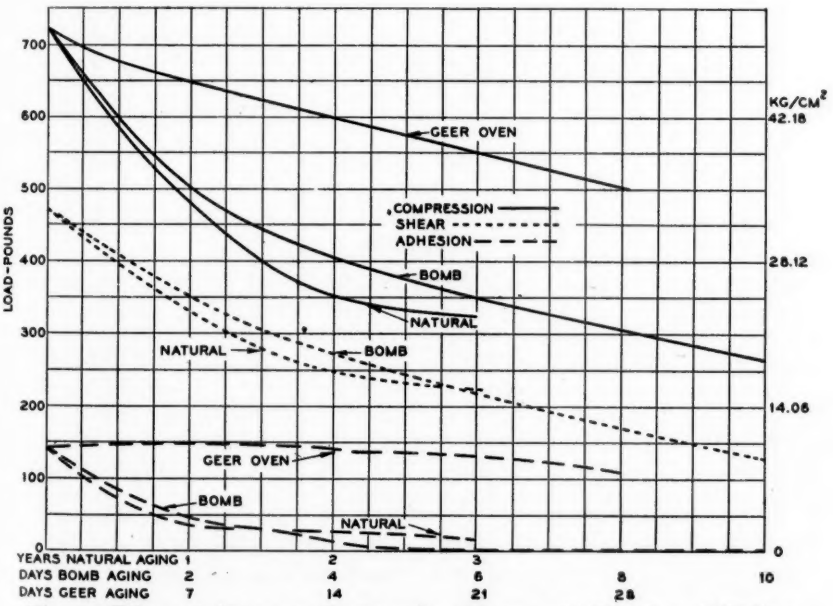

Fig. 3. Effect of Aging on Compression, Shear, and Adhesion of Rubber Insulation

An autographic record is traced on a card by the machine showing in detail the course of the compression or shear and the rupture. Figure 2 is a typical record showing these various components in the case of a 17 B. & S. gage rubber insulated conductor. The character of the curve traced, the sharpness of the rupture, and the thickness of the insulation at break indicate to a considerable degree the type of materials composing the insulation and their physical condition.

Figure 3 shows the comparative magnitude of the load factors involved in testing one type of rubber covered wire used with progressive aging, and Figure 4 shows averages of tensile, elongation, compression, and shear tests made on a large number of commercial insulated wires after bomb aging. Data are given on wire aged in the Bierer and Davis oxygen bomb for 3, 5, and 10 days at 70° C. and 300 pounds' oxygen pressure, wire aged in the Geer oven at 70° C. for 7, 14, 21, and 28 days, and wire subjected to natural aging for 6 months, 1, 2, and 3 years.

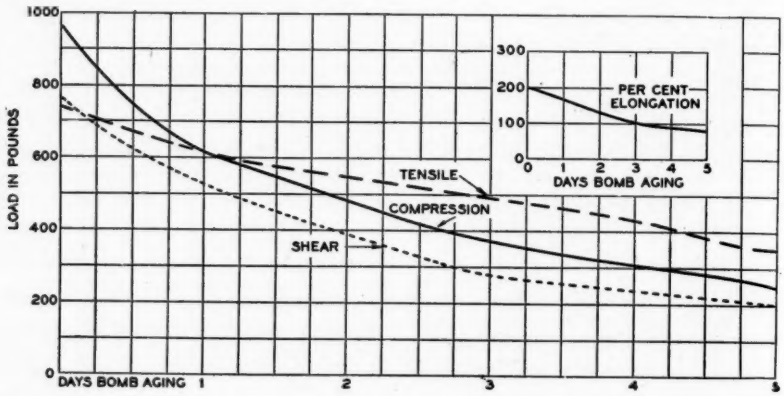

Fig. 4. Effect of Bomb Aging on Compression, Shear, Tensile, and Elongation. Average Values as Determined on a Number of Types of Commercial Rubber Covered Wire, 14 Gage Conductor, 5/64 Wall Insulation

The data in Figures 3 and 4 show that adhesion of insulation to conductor decreases rapidly on aging. This has been found to be true in service. Adhesion often is extremely variable, sometimes accounting for as much as 40 per cent of the original load. For this reason a more nearly true measure of the quality of the insulation is obtained by shear tests before and after artificial aging. It will be seen that for the type of rubber compounds in use on this wire artificial aging in the Geer oven is very slow, while aging in the Bierer and Davis oxygen bomb at 70° C. and 300 pounds' oxygen pressure corresponds fairly well with natural aging.

The Shear Test as a General Method for Evaluating Rubber

Aside from its use in testing rubber insulation for wire, for the past three years we have used the shear test generally in the course of evaluating all kinds of rubber stocks. The rubber test pieces have been standard molded or calendered sheets about 30 mils thick. These sheets were placed on the lower jaw of the machine and forced against a shearing member mounted in the fixed upper jaw. The shearing device consists, as in the insulation test, of a raised mandrel having a cutting edge two inches long with a suitable radius of curvature. It is, of course, apparent that the shearing load will be affected by the thickness of the rubber sheet and the shape and dimensions of the shearing tool. Figure 5 shows the relation of shearing load to thickness of rubber and to diameter of mandrel.

In Figure 6 is plotted the tensile product, shear resistance in pounds, and tensile strength of a series of compounds containing varying quantities of a mineral rubber having a softening point of 265° F. The base compound had the following composition:

Smoked sheets	15.0	Stearic acid	1.5
Reclaimed rubber	30.0	Sulphur	1.5
Zinc oxide	2.5	Accelerator	.5

The cure giving maximum tensile product was chosen in each case for test. For our purposes tensile product is taken as the product of tensile strength in pounds, and elongation in per cent divided by 100. Maximum physical properties are shown on both the shear curve and the tensile product curve for the same composition. The two curves correspond fairly well for practically all types of rubber compositions.

In Figure 7 are plotted tensile product, shear resistance, and tensile strength curves for a series of compounds based on the above formula in which whole tire reclaim was substituted for smoked sheets in the proportion of two parts reclaim for one part crude rubber. Again it is evident that the shear test simulates very closely tensile product.

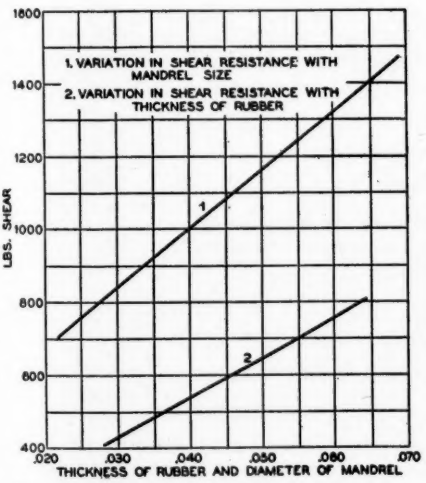

Fig. 5. Effect of Mandrel Diameter and Thickness of Rubber on Shear Load

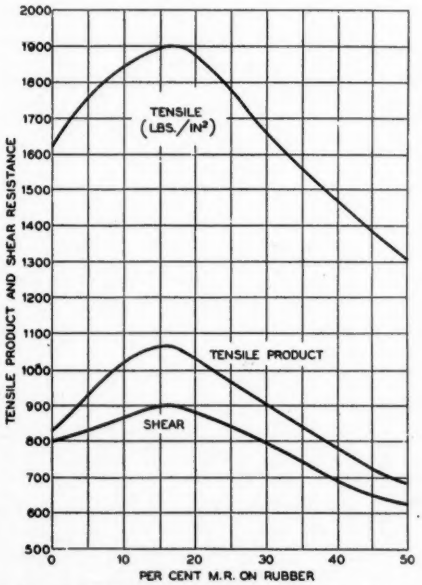

Fig. 6. Effect of M.R. on Tensile, Tensile Product, and Shear Resistance

The tensile product, shear resistance, and tensile strength for a series of compounds based on the above formula to which a clay filler has been added are plotted in Figure 8. It is of interest to note that small additions of filler cause an immediate drop in shear with very little change until about 30 per cent has been added, while tensile product and tensile per square inch show a straight line degradation in physical properties for each succeeding addition of loading material.

The values for tensile product have been found to correspond very well with

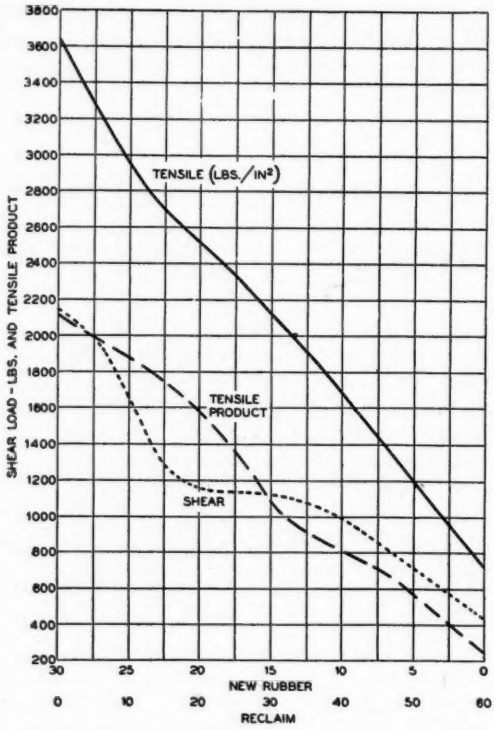

Fig. 7. Effect of Substitution of Reclaim for Smoked Sheet on Tensile, Tensile Product, and Shear

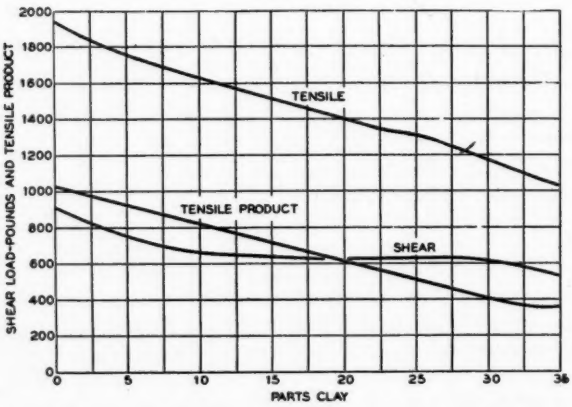

Fig. 8. Effect of Clay Loading on Tensile, Tensile Product, and Shear Resistance

the shear loads in a wide variety of rubber compounds such as tire treads, hose, packing, and heel stocks, and lead to the same relative rating of their merits. This method also differentiates between stocks containing such fillers as barytes, whiting, zinc oxide, and carbon black in a manner to give results comparable in value with those obtained by the tensile stress strain method.

The shear method has several advantages over the usual tensile methods.

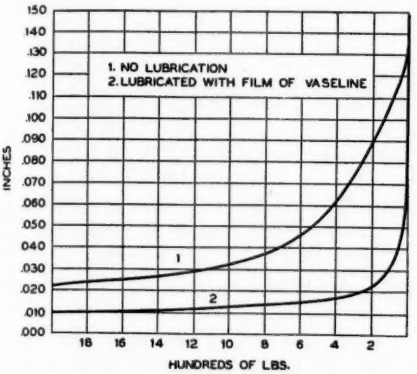

Fig. 9. Effect of Lubrication of Surface on Compression of a Pure Gum Stock

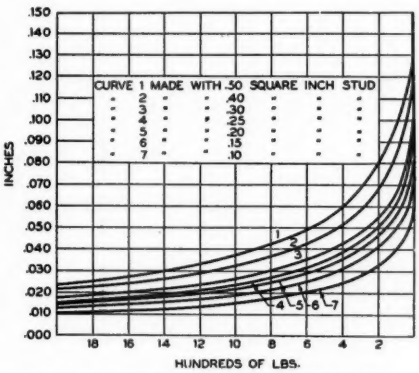

Fig. 10. Effect of Cross-Sectional Area of Compression Stud on Compression of a Solid Tire Stock Lubricated Surface

A sample of such size as to be unsuitable for the tensile test can be easily evaluated by the shear test and, in addition, the values obtained are not subject to variation in samples caused by slight defects such as cuts or agglomeration of filler particles to any marked degree.

Compression Testing of Rubber

As regards the general application of the machine to the compression testing of rubber, several methods have been employed. A flat piece of rubber, either circular or rectangular, has been placed between the flat jaws of the machine and compressed under various loads. Springs giving ultimate loads of both one and two thousand pounds have been used in the testing machine. Similar samples of rubber have also been compressed between the end faces of two cylindrical steel studs having diameters corresponding to those of the samples. The most promising method, however, appears to be that of forcing a cylindrical steel stud into a thick sheet or block of rubber.

The condition of the surface of the sample governs to a considerable extent the amount of distortion obtained with a given load. Figure 9 shows compression curves made with a steel stud having a diameter of 0.625-inch on a sheet of pure gum stock 150 mils thick with and without a lubricated surface.

Figure 10 shows different curves which were obtained on a specimen with studs of various cross-sectional area.

Compression curves entirely different from one another in character were obtained in testing the wide variety of commercial rubber stocks and other deformable materials available commercially. In Figures 11, 12, and 13 are shown compression curves for rubber tiling, a linoleum flooring composition,

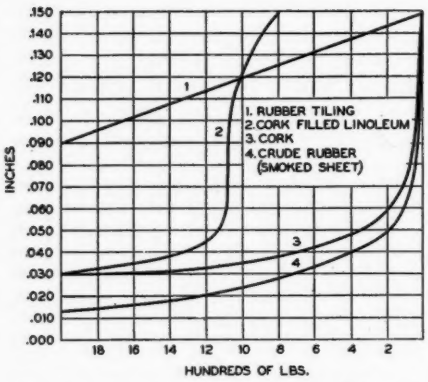

Fig. 11. Compression Characteristics of Various Materials

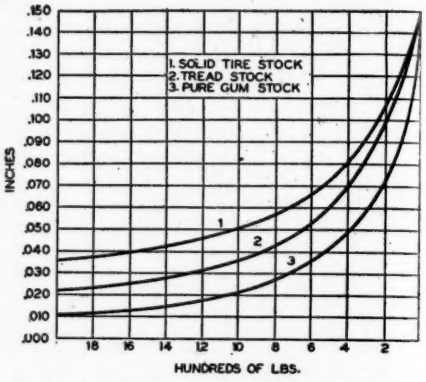

Fig. 12. Compression Characteristics of Various Rubber Compounds (Shelf Aged 6 Months)

cork, purified balata, smoked sheet, a solid tire compound, a tread compound, and a pure gum stock.

By quickly reversing the machine and repeating the compression curve the hysteresis quality of a specimen of rubber can be determined. This may prove to be of use in evaluating the properties of compounds employed under constant compression, for example for engine mountings in motor cars. In Figure 14 are shown compression and hysteresis curves for a tire tread compound.

Conclusion

1. A method for evaluating rubber covered wire by correlating compression, shear, and adhesion tests with bomb aging has been described.

2. It has been shown that the shear test described can be used for evaluating vulcanized rubber compositions with certain advantages over tests commonly in use.

3. Methods and some few data regarding the compression characteristics of several rubber stocks and other deformable materials have been given.

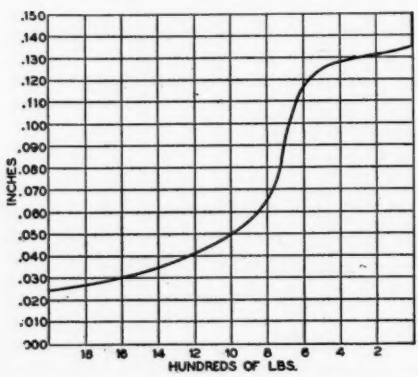

Fig. 13. Compression Characteristics of Pure Balata (Thickness 138 Mils)

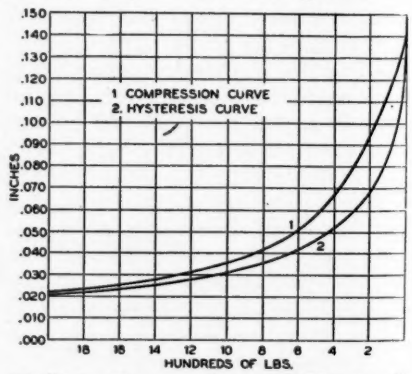

Fig. 14. Compression and Hysteresis Characteristics of a Tire Tread Compound

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The Strength and Stretch of Double Texture Rubber Goods

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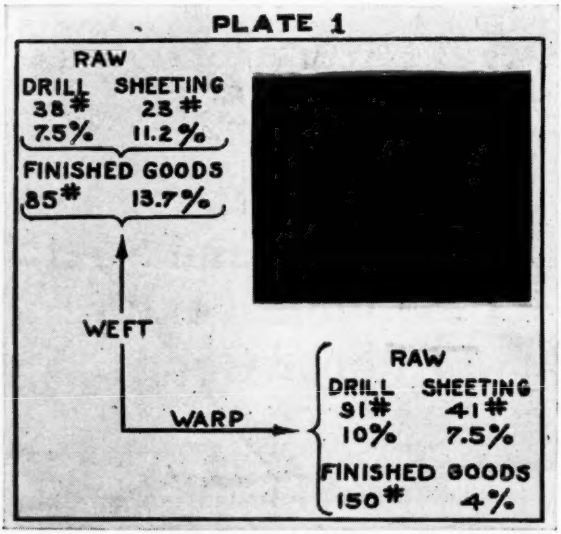
BOSTON WOVEN HOSE & RUBBER CO., CAMBRIDGE, MASS.

RUBBER articles may be divided roughly into three classes: (1) pure gum, (2) hard rubber, and (3) various combinations of rubber and textile fibers. This latter class is the largest and possibly the most important of the group, and includes besides tires the bulk of mechanical goods, such as hose, belting and sheet goods of various kinds. Probably no combination of useful materials affords a wider range of possibilities than the various combinations of rubber and textile fibers.

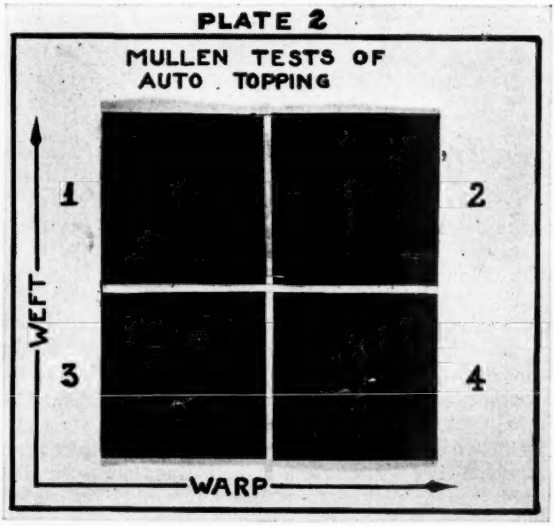
In rubber-textile combinations the cotton fiber is ordinarily used to impart tensile strength and to decrease the stretchiness of the product, while the attempt is made to retain at the same time as much resiliency as possible. Most of these combinations are of laminated construction, consisting of alternate layers of rubber compound and woven fabric, the physical properties being controlled by the construction of the fabric and the composition and cure of the rubber compound. Since cotton is usually more expensive on a volume basis than rubber, it is desirable to obtain the maximum tensile properties of the cotton fiber and to restrict its use as much as possible. That this is a difficult matter may be recalled when we compare the actual bursting strength of various mechanical goods with the so-called theoretical or calculated strength based on the additive strengths of the plied up fabrics in the fabricated article; it is at once apparent that only a small proportion of the fiber strength is effectively employed.

The most important consideration in designing plied fabrics to meet definite tensile specifications is to maintain *stretch balance* in



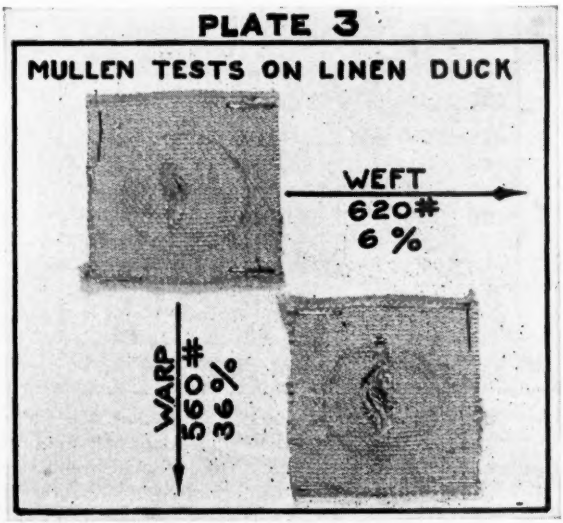
the various plies which go to make up the assembled article. Stretch balance means that the residual stretch in all plies of fabric is equal in any given direction. If this balance is maintained, every ply will do its share of work and should fail at the same instant if the plied fabric is stretched to the failure point. The stretch referred to is, of course, that of the plied fabric in the processed condition; stretch relationships in the grey goods condition have no significance, as changes in tensile-stretch properties take place during processing, curing, and because of contact with other plies in the finished article.

Automobile topping furnishes an interesting example of a plied fabric construction which is poorly designed to withstand actual service conditions. Plate 1 is a typical piece of two-ply auto topping which tests 150 lbs. total warp and 85 lbs. total weft as indicated. It may be concluded that since the weft is weaker than the warp it is more subject to failure in service, especially when subjected to the most common of injuries caused by pressure from a blunt instrument or by a blow. The reverse, however, is apparently true, and we can make use of the Mullen tester to illustrate the behavior of these types of fabrics in absorbing blows from blunt objects. When this type of fabric is placed in the Mullen tester and the pressure applied we obtain breaks in the topping fabric as shown in Plate 2. Four Mullen test pieces are shown. In the first one the diaphragm of the tester is just breaking through the warp. In the second sample the break has been further extended. The third sample shows the weft starting to tear, and in the fourth sample both warp and weft have completely failed. In spite of the fact that the warp is 75% stronger than the weft, it has broken first. The explanation of this effect is that the warp and weft do not take up the load evenly; the warp being compelled to take almost the entire load due to the stretchiness of the weft—consequently it has failed first,



followed by the weft. The total warp stretch is 4% compared with a total weft stretch of 13.7%. Had both warp and weft been constructed with the same percentage stretch, they would have taken up the load at the same rate and would have failed at the same time. The bursting strength would, therefore, have been greatly increased.

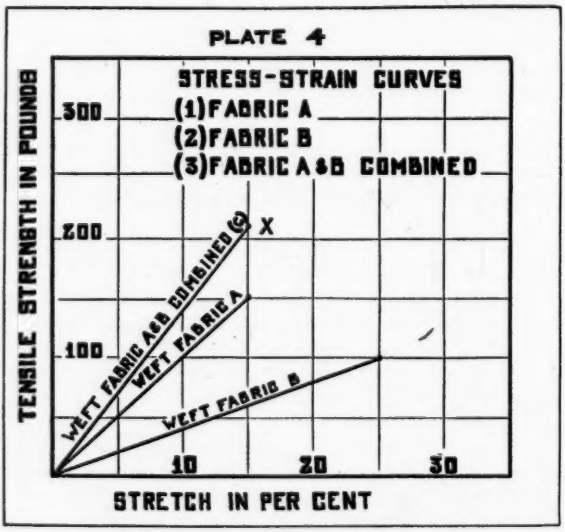
Plate 3 shows two Mullen test pieces of a very strong linen duck. Although the weft is stronger than the warp, it has failed in each case due to excessive stretch in the warp. Owing to the stretchiness of the warp, which is six-fold that of the weft, it never



reaches more than a nominal load of perhaps 100 lbs. by the time the weft has reached a breaking stress of 630 pounds. Tests of this character cannot, of course, be indiscriminately applied to all types of plied goods as many types require a different stretch or strength in either warp or weft, depending on the service conditions encountered.

Theoretically it should be possible to calculate the strength of a plied fabric construction, provided the tensile-stress characteristics of each individual ply is definitely known, and to design these fabrics with some degree of rationality. In determining the stress-strain characteristic of each ply, a sufficient number of tests must be made to eliminate the great variability of results encountered in fabric testing. The stress-strain for each ply must be that of the processed and cured fabric, and for use in computation can be obtained by combining two plies of the same fabric with warp and weft parallel, curing, testing, and dividing the tensile by the factor 2. The rubber compound used between plies and its gauge should be identical with that of the finished product whose strength characteristics it is desired to calculate. Having determined the ultimate tensile-stretch figure for a fabric in both warp and weft direction, the modulus can be plotted from this figure, and for purposes of approximation can be plotted as a straight line.

Referring to Plate 4, lines A and B represent the weft moduli of two fabrics which are plied together to form a laminated construction. If this laminated sheet is stretched in the weft direction the total stress would be expected to equal the sum of the stresses in both fabrics as shown in line C. As the fabric is stretched the

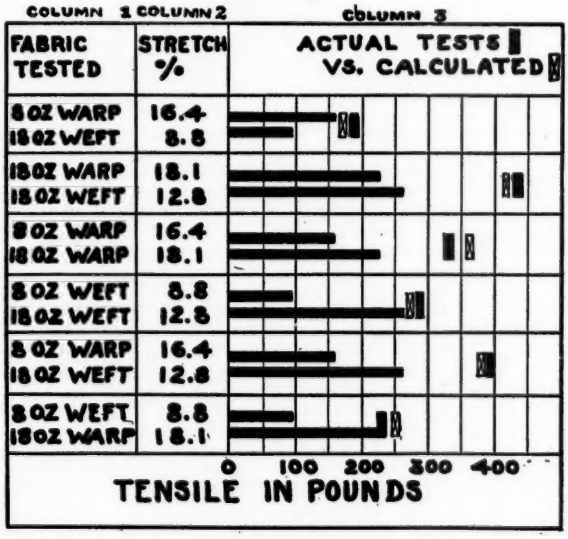


total stress would increase until point X is reached when fabric A would fail. The stress would not thereafter attain the value reached at X and would, therefore, represent the ultimate weft strength of the plied fabric. In other words the strength of fabric "B" is never fully realized as the combined fabric breaks before "B" is

fully stressed to its ultimate capacity. In connection with the testing of fabrics it should be noted that while laminated fabrics must fail ply by ply depending on the uniformity of stretch relationship, yet the time element between breaks is so short that it can seldom be detected, and failure usually occurs with suddenness.

In order to check the theory outlined above a series of two-ply rubberized fabrics were prepared and tested. The two fabrics chosen were an 8 oz. duck and 18 oz. duck and were selected to be widely different in tensile and stretch properties in both warp and weft. These were calendered, plied-up or doubled, and cured with the warp and weft of each oriented at a 90° angle to give varying test results. Plate 5 shows the different combinations of fabrics tested, and the actual tensile results compared with the calculated tensile strength. Column 1 shows the direction of ply yarns between testing machine jaws for each break recorded, i.e., in the first com-

PLATE 5



bination the 8 oz. warp and 8 oz. weft were combined in the same direction and tested in that direction. The second column shows the ultimate stretch percentage of each fabric in the combination when tested individually. In column three the horizontal lines, referred to in the scale below, show the actual tensile strength of each fabric when tested individually. The blocks in solid color show the actual laboratory tensile strength of the various combinations when plied up as shown and the blocks marked X show the calculated results as determined by the graphical method outlined in Plate #2. These results are in fair agreement and indicate that it should be possible, at least in the case of two ply combinations to calculate the tensile strength and to design such combinations with a better knowledge of their ultimate properties. In brief, the calculations are based on the assumption that when one fabric fails in a two ply combination, the ultimate strength of the combination is realized at that point. If, however, the ultimate strength of the

remaining fabric is greater than the combined stress in the two plies at the time of failure of the first, then the strength of the combination is no greater than for the second fabric alone. This is shown in Plate 5 in the combination of the 8 oz. weft and 18 oz. warp. It will be further noted that the maximum tensile results are obtained where the best "stretch balance" occurs as in tests Nos. 2, 3 and 5. Disregarding questions of precision, these results demonstrate that it should be possible to design plied fabric compositions with a fair expectation of obtaining the maximum properties of the textiles employed. To accomplish this result plied fabric constructions should be designed so that each fabric has the same residual stretch in any given direction. Fabrics should be specified and purchased with these considerations in view.

Unfortunately fabrics are not always plied up at 90° to each other. It is absolutely essential to resort to bias cutting in order to obtain certain stretch characteristics in certain rubber-textile combinations. Fabrics of this character are often poorly designed, in fact are not designed at all. These articles frequently fail to meet conditions of service and a vast quantity of cotton is wasted because its properties are never fully realized.

Plate 6 shows the construction relationship between bias cut fabrics when plied together to form a laminated construction. Fabric A is bias cut at about 30 degrees and is plied up with fabric B which is cut on the straight. For convenience we may call the angle which the warp of fabric A makes with the warp of fabric B the warp angle of the combination. When plied up fabrics of this character are stretched, a resulting stretch takes place in the warp and weft of both fabrics and certain readjustments in crimp take place which do not require consideration in this paper. Reference to Plate 7 indicates more clearly the changes which take place when a bias cut fabric is stretched. ABCD represents a section of fabric cut on a bias angle Θ. The section is so chosen that side AB is of unit length. If this fabric section is stretched X amount laterally and Y amount transversely, it will assume the proportions AEFK. The warp AC will stretch to the dimension AF as shown and the Weft BG will become BJ. Warp angle Θ changes to Θ^2 and a change also takes place in the fabric angle between warp and weft. The changes in length and stretch in warp AC and weft BG can readily be evaluated in terms of the original warp angle Θ and the lateral and transverse stretch, X and Y, for example

$AB = \text{unity} = 1$

$BC = \tan \Theta$

$AC = \sqrt{\tan^2 \Theta + 1} = \sec \Theta = \text{original warp length.}$

$AE = 1 + x$

$EF = \tan \Theta + y$

$AF = \sqrt{(1 + x)^2 + (\tan \Theta + y)^2}$

Stretch in $AC = AF - AC = \sqrt{(1 + x)^2 + (\tan \Theta + y)^2} - \sec \Theta$

$$\text{Therefore the \% stretch in warp } AC = \frac{\sqrt{(1 + x)^2 + (\tan \Theta + y)^2} - \sec \Theta}{\sec \Theta} (100) \quad \ldots\ldots (1)$$

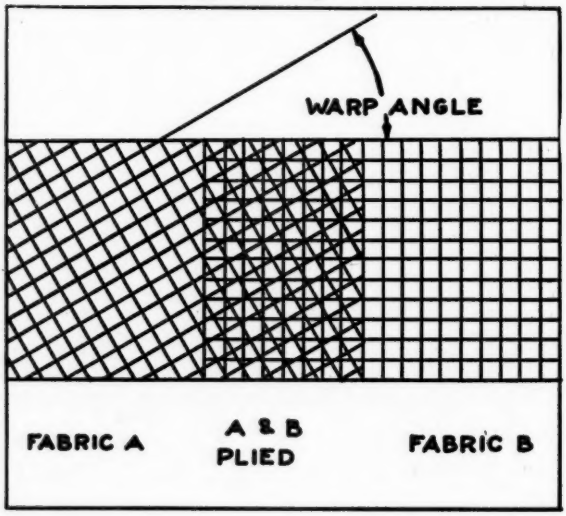
In a similar manner the stretch in the weft BG follows:

$$\text{\% stretch in weft } BG = \frac{\sqrt{[(1 + x)\ (\tan^2 \Theta)]^2 + (\tan \Theta + y)^2} - \tan \Theta \sec \Theta}{\tan \Theta \sec \Theta} (100) \quad \ldots\ldots (2)$$

In cases where the warp angle is greater than 45° the solution requires slightly different treatment due to point G falling within line AD and results in the following:

$$\text{\% stretch in weft } BG = \frac{\sqrt{[(\cot^2 \Theta)\ (\tan \Theta + y)]^2 + (1 + x)^2} - \csc \Theta}{\csc \Theta} (100) \quad \ldots\ldots (3)$$

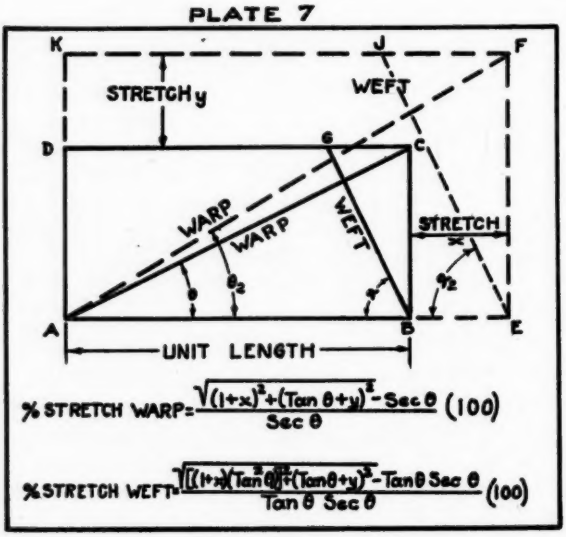
PLATE 6



When fabrics are tested in the laboratory the separating action of the testing machine jaw stretches the fabric until its ultimate strength is reached and failure takes place. The term stretch as used here is intended to mean the total elongation of the threads due to stretch in the cotton fiber, slippage between fibers, loss in crimp, and twist effects in yarn, ply yarn and cable.

The lateral stretching of fabrics in the testing machine jaws is

PLATE 7

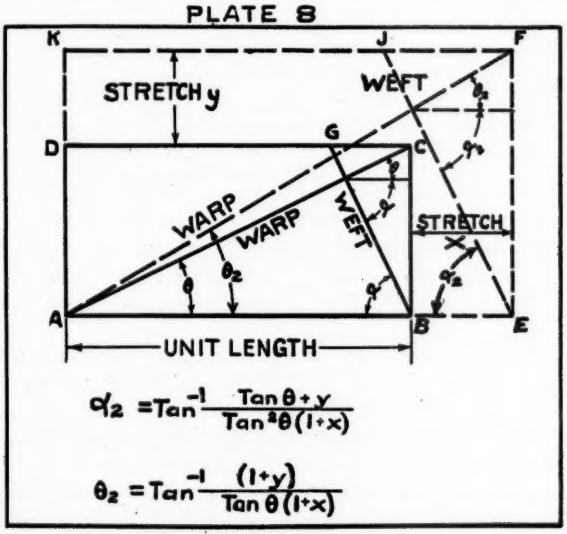


accompanied by transverse contraction and decrease in thickness which in general follows the equation: $(1 + x)\ (1 - y)^2 = 1$, where x is the elongation in percent and y the contraction percentage in both width and thickness. While an actual laboratory figure for each fabric investigated may be taken, for the purpose of approximation the above may be used. The transverse stretch y in the formulae proceeding, therefore, becomes $1 - \sqrt{\frac{1}{1+x}}$, the contraction being used as a negative stretch.

In cases where the fabric is placed in the testing machine jaws at an angle so that either warp or weft are at an acute angle or bias with the jaws, additional stretch in the fabric is permitted, due to change in angularity between warp and weft. When plied fabrics are tested in this manner, the stress required to produce failure should include that necessary to produce changes in angularity as well as that required for actual rupture of the fabric structure.

The stress necessary to produce a given change in angularity between warp and weft may be determined experimentally by stretching the fabric samples in the testing machine by the strip method and plotting the stress strain curve from the data obtained. The stress for a given deformation varies with the bias of the test sample with relation to the jaws of the testing machine, and is due

PLATE 8



partly to the inclusion of a variable number of ply yarns in the jaws when tested with a varying bias and partly to the fact that changes in angularity for a given jaw separation vary with the degree of bias of the sample.

The change in angularity between warp and weft which takes place on stretching bias cut samples may be calculated in terms

of the lateral and transverse stretch (or contraction). Reference to Plate 8 shows the changes which take place in angularity as the fabric is stretched a distance x laterally and y transversely as indicated.

In all cases before stretching the angle between warp and weft in any woven fabric is 90° or angle β. After stretching as shown it alters to β_2 while the bias angle changs from Θ to Θ_2. Angle β_2 equals $\Theta_2 + \alpha_2$ which may be evaluated as follows:

$$\Theta_2 = \tan^{-1}\frac{EF}{AE} = \tan^{-1}\frac{\tan\Theta + y}{1+x} \qquad \text{.....(4)}$$

Similarly

$$\alpha_2 = \tan^{-1}\frac{EF}{JF} = \tan^{-1}\frac{\tan\Theta + y}{\tan^2\Theta\,(1+x)} \qquad \text{.....(5)}$$

It is assumed that the total amount of work necessary to change the fabric angularity is constant for a definite change in angularity, regardless of the bias angle at which the fabric is stretched, and varies only with the number of warp and weft thread crossings.

In order to check the foregoing calculations and the assumptions on which they were based, a series of two-ply fabrics were rubberized, plied up at different warp angles with each other, cured and tested. The same fabric was used in both top and bottom plies and was 21. oz. duck selected because of widely varying properties of both warp and weft. The following shows the physical properties of this duck when tested in the rubberized and cured conditions.

	Warp	*Weft*
1. Tensile strength	270 lbs.	317 lbs.
2. Ultimate stretch in percent	28%	16%
3. Modulus of elasticity.....	9.7	19.8

(Note: tests by grab method, 1″ x 1″ x 3″)

In the experiments, five series of samples were prepared and tested as shown in Plate 9. At the same time the theoretical strengths were calculated and compared with the actual laboratory tests. The computations were carried out as shown below, and for exemplification, Sample 2 plied up at an angle of 30° is selected. In sample 2 the bottom fabric will be warpwise in the testing machine jaws and can, therefore, stretch 28% if permitted to do so by the top fabric, which lies at warp angle of 30° with the bottom fabric. The warp of the top fabric will obviously bear an extension of 28% in the direction shown, but the ultimate weft stretch of 16% will probably be the limiting factor, if any, in the extension of the test sample.

A. To calculate the stress in the warp of the bottom fabric

which is stretched as shown in Plate 9, use formula (1).

$$\frac{\sqrt{(1+x)^2+(\tan\Theta+y)^2}-\sec\Theta}{\sec\Theta}(100) = \%\text{ stretch warp} \quad (1)$$

where $x = 28\%$

$\Theta = 0$

$\tan\Theta = 0$

$$y = 1 - \sqrt{\frac{1}{1+x}}$$

$\sec\Theta = 1$ $\quad$ M_w = modulus of warp = 9.7

Since the bottom fabric is stretched on the straight the contraction y does not affect the length of the weft except as it affects the crimp and it will, therefore, be taken as zero for this case.

Substituting in (1) and solving, the % stretch = 28%. The stress in the warp of the bottom fabric is, therefore, 28 (M_w) = 28 (9.7) = 270 lbs.

B. To calculate the stress in the top fabric.

$\tan 30° = .577$ $\quad$ $\sin 30° = .5$ $\quad$ $x = .28$

$\sec 30° = 1.154$ $\quad$ $\cos 30° = .87$

$$y = 1 - \sqrt{\frac{1}{1+x}}$$

1. To calculate stress per inch width in top fabric warp.
   Substituting and solving in equation (1)
   % stretch warp of top fabric = 17.9%
   Stress per inch width of warp cross-section top fabric =
   17.9 (M_w) = 17.9(9.7) = 174 lbs.
2. To calculate stress in weft top fabric.
   Substituting in equation (2)
   % stretch in weft of top fabric = —6.3%
   Therefore the weft shrinks and shares no part in the total stress; it represents wasted cotton.

The stress per inch width crossection of warp and weft must be recalculated to represent the stress per inch width of combined fabric perpendicular to the testing machine jaws. It can be shown that the stress in this direction Swf is as follows:

$$Swf = Pw \cos^2\Theta + Pf \sin^2\Theta \quad (6)$$

where,

Pw = stress per inch width crossection of warp = 174 lbs.
Pf = stress per inch width crossection of weft = O
Θ = bias angle of cut.

Substituting and solving, Swf = 131 lbs.

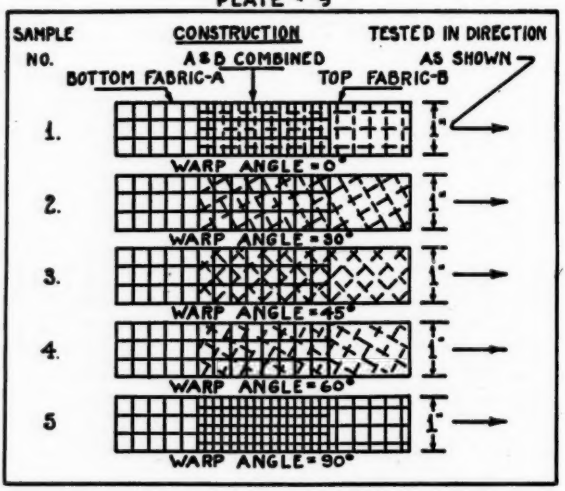
Therefore the total stress in the combined fabrics due stretching but not due to changes in angularity is as follows:

1. Stress in bottom fabric.....270lbs. per inch width
2. Stress in top fabric.....131 lbs. per inch width

Total.....401 lbs. per inch width

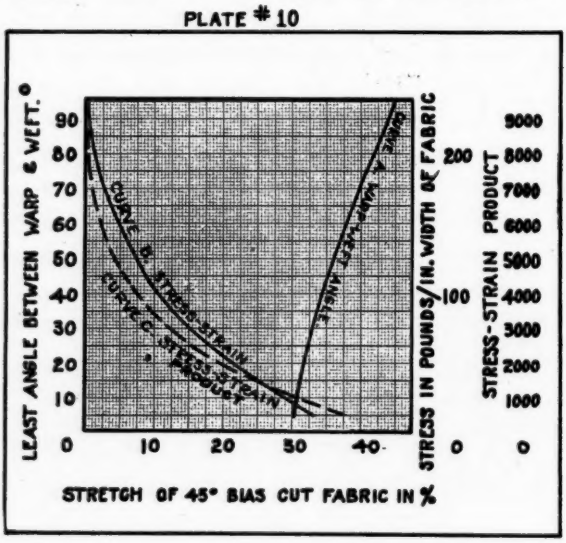
3. To calculate the stress due to change in angularity between warp and weft in the top fabric.

PLATE # 9



Reference to Plate 10 shows three curves. Curve A is an experimentally determined curve obtained by stretching a strip of the rubberized and cured fabric cut on a 45° bias and stretched to determine the distortion or change in angularity between warp and weft with relation to the percentage elongation of the strip. Curve B is the modulus obtained by stretching the strip and should represent the stress required to accomplish the changes in angularity between warp and weft. Actually it also includes the stress required to stretch the rubber in the combination as well as the small variable amount of stretch which may result in the fabric itself. In the low range of stretch required to effect relatively large angular changes the two latter effects may be neglected. It is

PLATE # 10



further assumed that the work necessary to effect a given change in angularity is constant. Curve C is a stress-strain product curve desired from and plotted to correspond to Curve B. Since the angularity changes from 90° to Θ_2 to $\Theta_2 + a_2$ where

$$\Theta_2 = \tan^{-1} \frac{\tan \Theta + y}{1 + x} = \tan^{-1} .357 = 19.6°$$

$$a_2 = \frac{\tan \Theta + y}{\tan^2 \Theta (1 + x)} = \tan^{-1} 1.075 = 47.1°$$

Total.....66.7°

So that the resulting acute angle between warp and weft changes from 90° to 66.7°. Referring to curve A, the elongation in percent on a 45° bias cut corresponding to a warp-weft angle of 66.7° is 31.5% stretch. Referring to curve C a stretch of 31.5% on 45° bias corresponds to 2200 work units, and since the fabric is actually stretched 28% at 30° bias the stress corresponding to the work done should approximate 79 lbs. The total stress in the sample at the point of failure should then approximate:

1. Stress in bottom fabric per inch width..... 270 lbs.
2. Stress in top fabric per inch width..... 131 lbs.
3. Stress in top fabric due to change in angularity..... 79 lbs.

Total stress at failure point..... 480 lbs.

Table No. 11 shows the laboratory test results obtained in comparison with the calculated results obtained as outlined above.

TABLE 11

	Warp angle of top to bottom fabric	Calculated tensile strength	Laboratory tensile strength
1.	0°	540*	540
2.	30°	480	510
3.	45°	487	525
4.	60°	470	526
5.	90°	472	440

*Laboratory results used as basis for subsequent calculations.

It is apparent from the foregoing conclusions that the specifications for rubber-textile combinations should receive more careful consideration with a view to obtaining the maximum properties of each ply through the use of approximate calculations to determine the probable strength and stretch. If it is asked why some fabrics are cut on the 45 degree bias instead of 46 or 47 degrees, a rational answer will not likely be obtained. It is obvious that the strength and stretch characteristics of certain classes of merchandise should be calculated approximately and the fabrics purchased on a stretch as well as a tensile strength basis. If this is done, the savings in cotton alone will be enormous and the quality of the various products will be correspondingly improved.

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Vol. 27, No. 7, July 10, 1930.]

Laboratory Flexing Tests as An Aid in Investigating the Pneumatic Tire Carcass

By H. A. DEPEW and H. C. JONES

The New Jersey Zinc Company, Palmerton, Pa.

TIRE tests, both service and test wheel methods, are generally used for carcass development, supplemented to a limited extent by laboratory tests, which include stress-strain tests on the compound and the cord, friction tests to measure the force necessary to pull the rubber compound from the cord, and pulley flexing tests. Owing to the cost and difficulty of reproduction of tire tests, it is desirable to use laboratory tests in so far as possible, although it will be impractical to eliminate tire tests as final checks before putting laboratory information into production and as a general method of attack for special problems in design. Among the important problems that lend themselves especially well to laboratory methods are: (1) Insulation of tire cord, including thickness of skim and spacing of the cord; and (2) rubber compounds (both before and after aging), including composition and state of cure.

In choosing laboratory methods, it was decided to use flexing methods, with tension tests on the compound as an aid in judging state of cure. Friction tests were not made since they would be meaningless for indicating the bond between rubber and cotton when the cords are well separated in rubber.

The test pieces chosen were six-ply cord belts 9 in. long and 1 in. wide, with three layers of cord running lengthwise and three alternate layers crosswise. These belts were assembled and vulcanized according to the methods described by Gibbons.[1] Belts are not

NOTE: This paper was presented at the Thirty-third Annual Meeting of The American Society for Testing Materials, held at Atlantic City, N. J., June 23-27, 1930, and is reprinted herein with the permission of the Society.

[1] *Industrial and Engineering Chemistry* (Analytical Edition), Vol. 2, No. 1, p. 99 (1930).

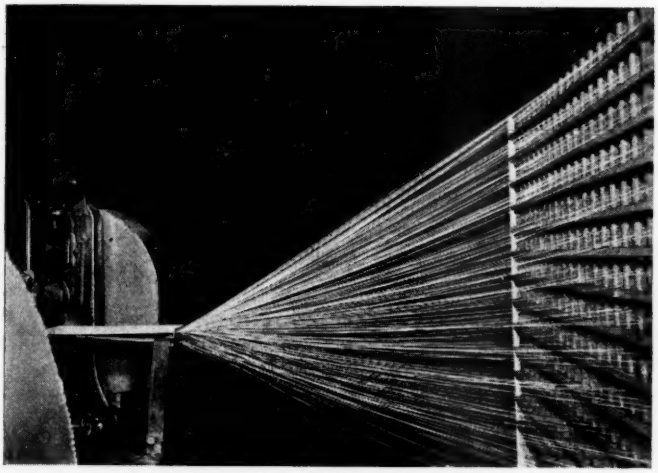

Fig. 1.—Rubber Impregnated Cord Feeding from Small Bobbins Through Combs to the Calender Where They Become Imbedded in a Sheet of Rubber

tested until after five days' storage since the flexing life is relatively short immediately after vulcanization and it increases for from one to five days before becoming constant, depending on the compound.

A ply thickness of 0.050 in. in a six-ply belt 9 in. long and 1 in. wide corresponds to a volume of rubber compound of 2.01 cu. in. when 17 cords per inch are used, and to a volume of rubber compound of 1.68 cu. in. when 25 cords per inch are used. The additional volume of rubber for thicker plies can be calculated directly from the area and the additional thickness.

The details of coating the cord with a rubber compound are briefly described with the belief that they will be helpful. The tire cord, received on large bobbins, is dried and passed through a rubber cement, consisting of the compound dissolved in benzene. After drying, the cord is rewound on small bobbins and fed through two combs to a three-roll calender and skimmed on one side (Fig. 1). The compound used in skimming is the same as that used in making the cement. The rubber sheet with the cords firmly in place is again passed through the calender and skimmed on the other side to the desired gage. When the stock cools, it is cut into squares, piled up, and cured according to the method of Gibbons.[1]

Methods of Flexing

The belts are tested on three types of flexing machines: (1) pulley test (constrained bending); (2) free bend test; and (3) jerking test. The pulley test is well-known and the other two are experimental tests.

Pulley Test:

The United States Rubber Co. flexing machine built for the Society's Committee D-11 on Rubber Products by the Henry L. Scott Co., is used for the pulley test (Figs. 2 and 3). In this test, the small belt is made to conform to a 9/16 in. pulley and repeatedly flexed (175 cycles per minute) under a specified load of 150 lb. (68.2 kg.). The belt tension is computed to be 81½ lb. (37 kg.) rather than 75 lb. (one-half of the 150-lb. load), since the pull on the ends of the belt was not exactly vertical.

Free Bend Test:

In tire service, the contour of the flexing bend is not fixed, but depends somewhat on the stiffness of the belt. In an article on balloon tires,[2] Hale showed a picture of a tire in service where the side wall had actually folded back on itself. The tire shown was probably a 21/7.30 carrying 20 lb. of air, and the flexing was extreme. Folding puts the side wall under compression at one point and the free bend is simulated (Fig. 4) by gripping the test belt

[2]*Journal*, Soc. Automotive Engrs., Vol. 13, No. 1, p. 41.

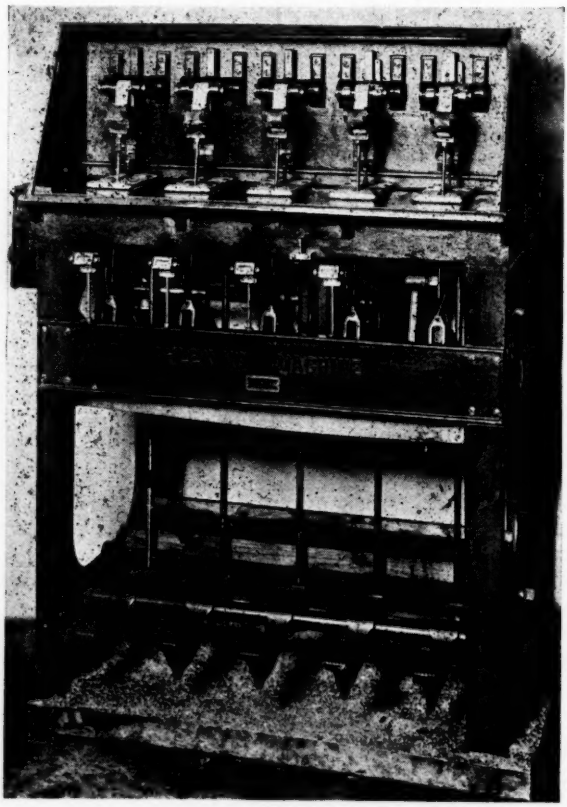

Fig. 2.—Pulley Flexing Machine

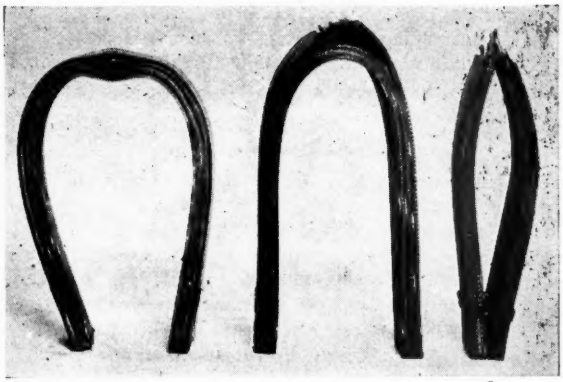

Fig. 3.—Typical Pulley Flexing Failures

If a 100-lb. load had been applied rather than the 150-lb. (68.2 kg.) load, and only belts with 25 ends had been used, all the failures would have been due to separation.

in jaws at the two ends and moving them back and forth with a reciprocal motion at high speed (1150 cycles per minute).

Jerking Test:

In addition to tire failures from separation, there are failures due to cord breaks and the ability of the cotton to withstand repeated stress is of considerable importance. With this in view, a

Fig. 4.—Free Bend Flexing Machine

jerking test was introduced. This test (Fig. 5) is intended to simulate the loading strains induced in a tire carcass in service. A dead weight applies a load which corresponds to the cord tension produced by the air pressure within the tire. Road blows, which are superimposed in service, are comparable to the force applied by the crank arm through the coil spring. The cord tension in the jerking test varies from a constant load of 0.89 lb. (0.40 kg.) per cord to a maximum intermittent load of 5.48 lb. (2.49 kg.) per cord. Belts with 17 cord ends per inch are under a constant tension of

45.2 lb. (20.55 kg.) and a maximum intermittent load of 280 lb. (127.4 kg.). The belt tension using 25 ends per inch is 66.4 lb. (30.2 kg.) constant load and 413 lb. (188 kg.) maximum intermittent load. In the jerking test, the belt is not supported vertically due to the development of failures in the jaws.

Results and Discussions

Table I gives data showing the range of reproducibility of the results of the three tests.

Table II (summary of detailed data given in Figs. 6, 7, and 8) shows that an increase in ply thickness and a decrease in the number of ends within the limits investigated increases the pulley flexing life; or in other words, it might be stated that with more rubber between the cords (better insulation from one cord to another), the pulley flexing life is increased. Better insulation of cords is gen-

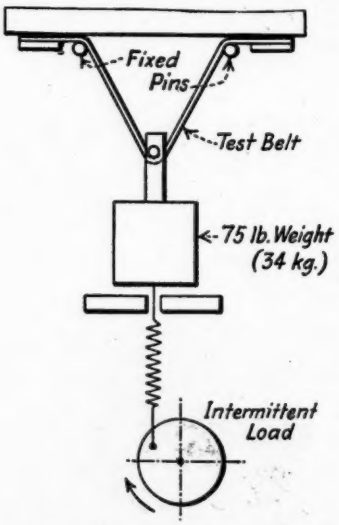

Fig. 5.—Diagram of Jerking Test

TABLE I.—REPRODUCIBILITY OF RESULTS.

Tests on Belts Cut from the Same Pad

Test	Pulley Flexing Test, cycles	Free Bend Test, cycles	Jerking Test, cycles
No. 1	30 600	57 100	62 100
No. 2	33 100	51 700	65 500
No. 3	31 000	54 600	63 200
No. 4	33 900		

REPEAT PULLEY FLEXING TEST MIXING NEW BATCHES OF THREE DIFFERENT COMPOUNDS[3]

	Compound A	Compound B	Compound C
Original Test	37 400 cycles	38 500 cycles	25 200 cycles
Repeat Test	37 600 "	43 900 "	27 700 "

[3]Each value is the average of four pulley flexing tests.

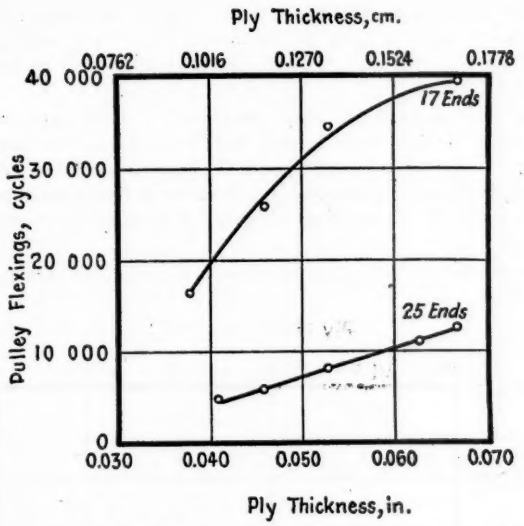

Fig. 6.—Showing the Influence of Ply Thickness and Number of Ends on Pulley Flexing Life

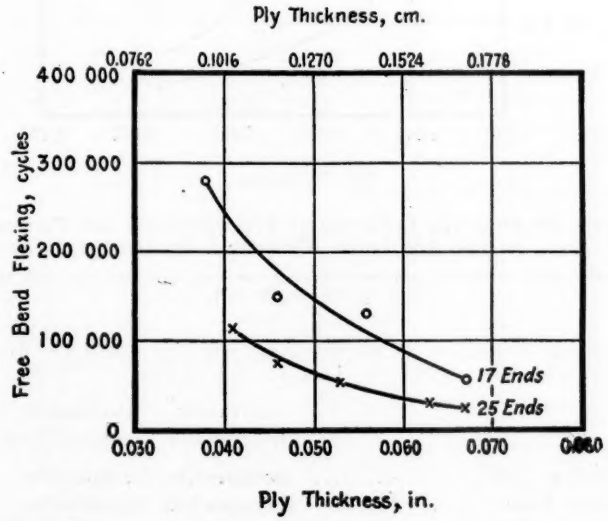

Fig. 7.—Showing the Influence of Ply Thickness and Number of Ends on Free Bend Flexing

erally recognized to give longer tire life, especially in the case of heavy-duty tires. Accordingly, there is a strong indication that the pulley flexing test is a guide to the flexing life of present-day tires as stated by Gibbons, and it is an especially applicable method for heavy-duty tires.

It has been pointed out that when very low air pressures are used, the tire section tends to flex with more of a free bend; accordingly, in any development work looking toward the adoption of extremely low air pressures, the free bend test should be considered. Table II shows that although a decrease in number of

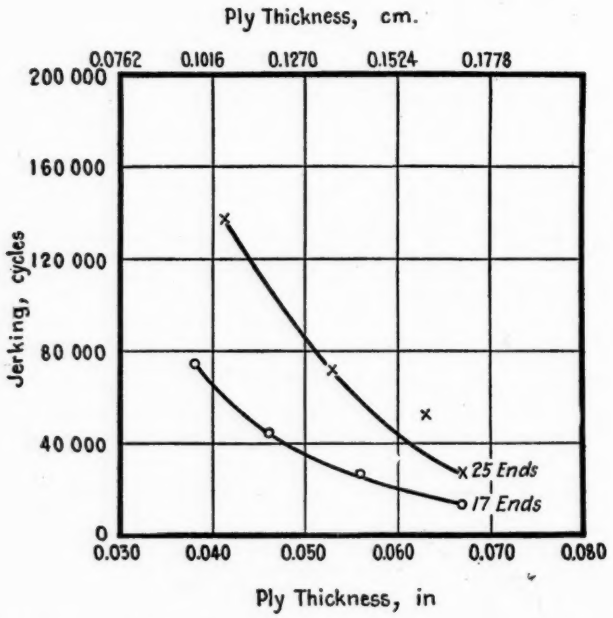

Fig. 8.—Showing the Influence of Ply Thickness and Number of Ends on the Ability to Withstand Repeated Jerking

The tests were made with the same tension per unit cord and not with the same tension on the belt.

TABLE II.—EFFECT OF INCREASED INSULATION OF CORDS ON BELT LIFE.

	Increase in Ply Thickness	Decrease in Number of Ends
Pulley Test	increases life	increases life
Free Bend Test	decreases life	increases life
Jerking Test	decreases life	decreases life

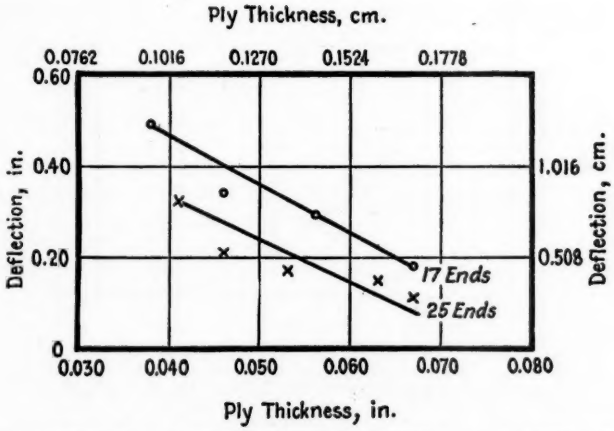

Fig. 9.—Showing the Influence of Ply Thickness and Number of Ends on the Stiffness of the Belt

The test was made by resting the 1-in. (2.54-cm.) wide belt over two supports 6 in. (15.25 cm.) apart and placing a load of 0.44 lb. (0.2 kg.) at the center and measuring the deflection at that point.

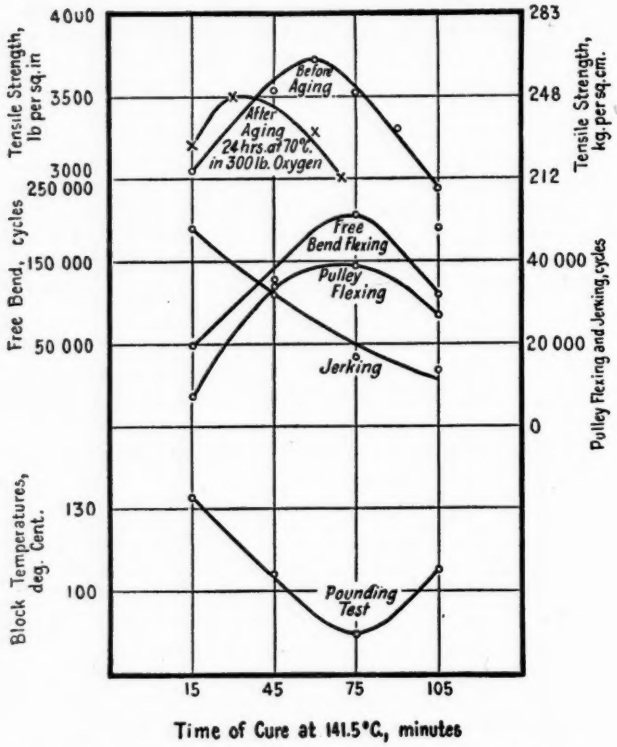

Fig. 10.—Showing the Influence of Cure

Seventeen-end belts with a ply thickness of 0.053 in. (0.135 cm.).

ends increases the belt life, an increase in ply thickness decreases the life. Examination of the belt during flexing indicates that compressive forces on the inside of the bend of the thicker belts cause failure.

From the above information it would be logical to expect a thick side wall super-tire to break down badly when run flat since free-bend flexing is approximated, and the authors believe that this is the general experience of motorists.

The value of the jerking test for determining the kind and amount of cotton is shown by determining the comparative jerking life of a 25-cord-end belt with that of a 17-cord-end belt under a jerking tension ranging from 45.3 lb. minimum to 280 lb. maximum. The 25-end belt lasted for 11,385,000 cycles whereas the 17-end belt withstood only 13,000 cycles.

In order to investigate the effect of the amount of insulation of the cords when different numbers of cord ends are used, the total belt tension is adjusted as described earlier so that the average individual cord tensions are equal. The tests (Fig. 8) show that the

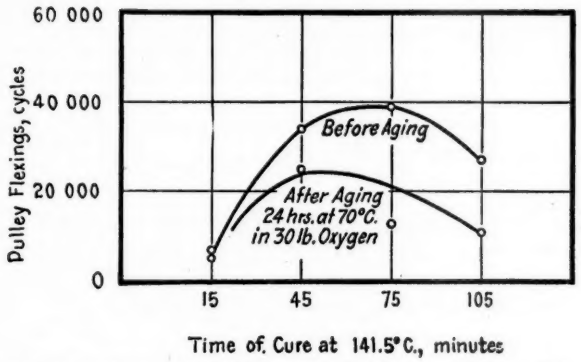

Fig. 11.—Showing the Influence of Aging on Pulley Flexing Over a Range of Cures

Seventeen-end belts with a ply thickness of 0.053 in (0.135 cm.).

best jerking life is obtained when the cords are poorly insulated; that is, with a maximum number of ends and a minimum ply thickness. It is apparently desirable to reduce the movement of the individual cords relative to one another to a minimum.

It should be kept in mind that continual flexing weakens the cords and that a tire with low cotton strength might have sufficient strength for all emergencies if the cords were not weakened due to poor flexing qualities.

The behavior of the test belts in the three tests is influenced to a considerable extent by the stiffness of the belt. The stiffness is determined by the amount and kind of rubber compound. For completeness, the effect of ply thickness and number of ends on stiffness is shown in Fig. 9.

Effect of State of Cure:

The tests shown so far have been made at a practical technical cure; namely, 45 minutes at 141.5° C. for the following compound:

Smoked Sheet	460 g.
Pale Crepe	460 g.
Sulfur	37 g.
Mineral Rubber	45 g.
Stearic Acid	4.5 g.
Medium Pine Tar Oil	18.0 g.
Age-rite Resin	18.0 g.
D. O. T. G.	9.0 g.
Red Label Kadox	280.0 g.

The effect of state cure is shown in Fig. 10. The maximum tensile strength for the compound comes at the 60-minute cure for the unaged stock and at the 30-minute cure for the aged stock. Superior flexing by the belts comes at an over-cure (75 minute). Test blocks of the compound subjected to repeated pounding[4] heat

[4]H. A. Depew and E. G. Snyder, "The Use of a Group of Performance Tests for Evaluating Rubber Compounds that must Withstand Repeated Compression," *Proceedings*, Am. Soc. Testing Mats., Vol. 29, Part II, p. 962 (1929). RUBBER AGE (N. Y.), Vol. 25, p. 371 (June 10, 1929).

up and reach an equilibrium temperature which is a minimum for the 75-minute cure—the same cure that gives the best flexing. Since a resilient stock heats to a minimum, it is reasonable to assume that resiliency in a compound is one important consideration in choosing a tire carcass compound.

The apparently anomalous results of increased jerking life with decreased cure are possibly due, in part, to flow of the plastic under-cured rubber compound allowing better equalization of tension among the cords.

The influence of aging on the pulley flexing life is shown in Fig. 11. Over the range of cures, there is an appreciable reduction in flexing life.

Effect of the Composition of the Compound:

The flexing method of investigation has been applied to the problem of choosing rubber compounds for the pneumatic tire carcass. Two compounds that tested about 100 per cent apart in the pulley test when using a belt built with 17 ends and a thick ply were approximately equal when 25 ends and a thin skim were used. Good insulation of the cords accentuates differences in ply separation, and therefore good insulation is the preferred condition when testing compounds for ply separation. This influence of belt construction on flexing life with different compounds emphasizes the importance of studying tire construction in connection with the compounding of the pneumatic tire carcass.

[From Journal of the Washington Academy of Sciences, Vol. 20, No. 12, pages 213–23, June 19, 1930.]

The Compressibility of Rubber

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Although many of the elastic properties of rubber have been investigated with very interesting results, no measurements have been made, so far as we know, of its cubic compressibility at high pressures. Those measurements which have been made at low pressures yield results varying from 93×10^{-6} obtained by Clapeyron[1] to an estimate of the order of the compressibility of bronze (about 1×10^{-6}) given by Amagat.[2] As the compressibility of rubber enters as a minor correction into most compressibility measurements at high pressures, it is very desirable to have a reliable estimate of its value. In this communication we propose to give the results of experimental determinations of the compressibility at 25° of three samples of rubber which were furnished to us by H. L. Curtis and A. H. Scott of the U. S. Bureau of Standards.

The samples are described as follows:

Sample A.—Hard rubber from panel made by the Goodrich Company. It is a rubber-sulfur compound containing no inorganic fillers. The total sulfur amounts to 27.4 per cent. of which 0.21 per cent. is free sulfur. The density is 1.149 at 27° C.

Sample B.—A rubber-sulfur compound containing 90 per cent. smoked rubber and 10 per cent. sulfur and vulcanized 105 minutes at 300° F. Density = 0.990 at 25°.

Sample C consists of pale crepe rubber 90.75 per cent., zinc oxide 5 per cent., sulfur 4 per cent., tetramethylthiuram disulfide 0.25 per cent. It was vulcanized for 30 minutes at 260° F. Density = 0.990 at 27°.

Samples B and C were called soft rubber.

The samples of rubber were cut into discs and built up to form cylinders approximately 20 cc. in volume. On such specimens were the compressibility measurements made. The technique employed for such measurements in this Laboratory has already been described in detail,[3] and may be summarized as follows. The rubber was placed in a heavy-walled steel cylinder and completely surrounded by a suitable liquid. The volume of the liquid was then diminished by forcing a special piston into the cylinder and the pressure so generated read to one bar[4] by an electrical resistance gauge. The travel of the piston, which was a function of the decrease in volume, was measured by a dial micrometer gauge. The apparatus was calibrated at frequent intervals with a substance whose compressibility is accurately known, *viz.*, cold-rolled steel.[5] In this way adequate corrections for the compressibility of the pressure-transmitting liquid, for the stretching of the bomb, and for the distortion of the packings were made.

[1] *Compt. rend.*, **46**, 208 (1858).

[2] Cf. Lundal, *Ann. Physik*, **66**, 741 (1898).

[3] Adams, Williamson and Johnston, *J. Am. Chem. Soc.*, **41**, 12 (1919); Adams and Williamson, *J. Franklin Inst.*, **195**, 475 (1923).

[4] 1 bar (b.) = 10^6 dynes/cm.^{2} = 0.987 atmosphere. According to the "International Critical Tables" this is the only internationally accepted use of the word "bar," although it has been used to mean 1 dyne per sq. cm. We advocate the more general use of the word bar instead of megabarye, which we have hitherto employed, to indicate 10^6 dynes/cm.^{2}, particularly because of the convenience of the term "kilobar" which denotes one thousand bars (approximately 1000 atm.) and is the logical high-pressure unit.

[5] P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **58**, 166 (1923).

All readings were made by adhering rigorously to a definite procedure. The pressure was first raised to 12,400 bars and then lowered to about 50 b. below 12,000. A pause was made for temperature readjustment and then the pressure slowly raised to as near 12,000 b. as possible. After the piston displacement had been read, the pressure was lowered to 10,950 b. and after a pause brought back to 11,000 b. A reading was made and the process repeated for successively lower pressures at interva's of 1000 b. Unless a definite procedure is followed in all the experiments, serious errors from hysteresis in the bomb and packings are apt to be introduced. Especially necessary is it that the runs with the specimen under investigation be made exactly like those with the standard steel.

Results.—The experimental observations which consist of two series of pressure and piston displacements, one for the rubber and one for the steel, are converted by a calculation which has already been described[6] to a single table of pressures (Table I) and the corresponding values of $-\frac{\Delta V}{V_0}$, the fractional change in volume of the rubber, $-\frac{\Delta V}{V_0}$ being zero at 2000 b. Column A refers to the hard rubber, Column B to the rubber containing 10 per cent. sulfur, and Column C to rubber with 4 per cent. sulfur.

In order to smooth the results and to determine the volume change and compressibility at any pressure it is our custom to express $-\frac{\Delta V}{V_0}$ as a function of pressure—usually as a function of $(p-2000)$. With most solids this is comparatively simple, as a linear or quadratic equation fitted to the data by the method of least squares represents the observations very exactly.

TABLE I
EXPERIMENTAL RESULTS

$$-\frac{\Delta V}{V_0} \times 10^2 \text{ (Obs.)}$$

Pressures in bars (p)	A	B	C
12000	10.085	10.463	11.222
11000	9.442	9.864	10.608
10000	8.733	9.217	9.922
9000	7.994	8.528	9.200
8000	7.177	7.780	8.410
7000	6.267	6.967	7.535
6000	5.255	6.010	6.498
5000	4.129	4.925	5.233
4000	2.903	3.566	3.779
3000	1.514	1.940	2.056
2000	0.000	0.000	0.000
1000	− 1.692	− 2.442	− 2.682

The volume changes produced when rubber is compressed hydrostatically can not be represented by a quadratic equation. Indeed, the compressibility of rubber is more like that of a liquid than of a solid. At low pressures the compressibility is very high but it falls off rapidly at the higher pressures, the behavior being closely akin to that of a liquid. Up to the present no satisfactory equation has been devised for expressing $-\frac{\Delta V}{V_0}$ for liquids as a function of the pressure over any considerable range of pressures.

[6] Adams and Williamson, *J. Franklin Inst.*, **195**, 475 (1923); Adams and Gibson. *Proc. Nat. Acad. Sci.*, **12**, 275 (1926).

Among others,[7] three equations involving four constants each were tried: (*a*) a cubic, (*b*) an hyperbola, (*c*) an exponential function. These three equations will not be discussed.

(*a*) *Cubic Equations.*—The first equation tried was of the form:

$$y = a + bx + cx^2 + dx^3 \qquad (1)$$

where, as throughout this paper, $y = -\frac{\Delta V}{V_0} \times 10^5$ and $x = \frac{p-2000}{1000}$. It was fitted to the three sets of results by the method of least squares. The results are summarized in Table II where the figures in the column labeled "obs.-calc." refer to the difference between the observed value of y (Table I) and those calculated by the following equations:

$$y = -4 + 1603.4x - 80.67x^2 + 2.121\ x^3 \qquad (1A)$$
$$y = 18 + 2075.0x - 169.52x^2 + 6.677\ x^3 \qquad (1B)$$
$$y = 8 + 2199.3x - 170.15x^2 + 6.2535x^3 \qquad (1C)$$

TABLE II

REPRESENTATION OF RESULTS BY MEANS OF CUBIC EQUATIONS

	Sample A		Sample B		Sample C	
p	$-\frac{\Delta V}{V_0} \times 10^2$ (Calc.)	Obs.-Calc. $\times 10^4$	$-\frac{\Delta V}{V_0} \times 10^2$ (Calc.)	Obs.-Calc. $\times 10^4$	$-\frac{\Delta V}{V_0} \times 10^2$ (Calc.)	Obs.-Calc. $\times 10^4$
12000	10.084	0.1	10.493	3.0	11.240	− 1.8
11000	9.439	0.3	9.830	3.4	10.579	2.9
10000	8.746	−1.3	9.188	2.9	9.914	0.8
9000	7.995	−0.1	8.527	0.1	9.211	− 1.1
8000	7.170	0.7	7.807	− 2.7	8 430	− 2.0
7000	6.261	0.6	6.990	− 2.3	7.532	0.3
6000	5.255	0.0	6.033	− 2.3	6.483	1.5
5000	4.137	−0.8	4.897	2.8	5.244	− 1.1
4000	2.897	0.6	3.543	2.3	3.776	0.3
3000	1.520	−0.6	1.930	1.0	2.043	1.3
2000	− 0.004	0.4	0.018	− 1.8	0.008	− 0.8
1000	− 1.690	0.2	− 2.233	−20.9	− 2.367	−31.5

Equation 1A represents the observations on hard rubber very satisfactorily. The deviations are so small that it was felt that no further computations were necessary for the hard rubber results.

It appears, however, that a cubic equation does not give a good representation of the volume changes under pressure for the two samples of soft rubber, the worst feature being the apparent failure of the equations at the top and bottom of the table. The large deviation at 1000 b. illustrates this clearly and if $\frac{dy}{dx}$ obtained by differentiating Equation B is plotted against x it will be seen to pass through a minimum at 10,000 b., a circumstance which is most improbable.

We might conclude by saying that a cubic represents the fractional change in volume of hard rubber as a function of pressure very well, but that a cubic equation may only be used as a short interpolation equation with the two soft rubbers.

(*b*) *Hyperbolic Equations.*—An equation of the type

$$y\ (x + \text{const.}) = a + bx + cx^2 \qquad (2)$$

was applied to the data for Samples B and C. The results, given in Table III and calculated with the following equations are disappointing:

[7] Several other types of equations, based on the published equations of state, were tried but the results were not as good as those for the three equations which are discussed here.

$$y\,(x + 8.0) = \quad 293 + 17290.4x + 145.83x^2 \qquad (2B)$$

$$y\,(x + 8.0) = -206 + 18883.8x + 130.61x^2 \qquad (2C)$$

(*c*) *Exponential Equations.*—The large decrease in volume at lower pressures which diminishes at high pressures suggests an equation of the type

$$y = A + Bx + C\,(1-e^{-}) \qquad (3)$$

As x gets large the last term of the equation approaches zero and we are left with the equation

$$y = A + Bx.$$

TABLE III

REPRESENTATION OF RESULTS FOR TWO TYPES OF SOFT RUBBER BY A HYPERBOLA

	Sample B		Sample C	
p	$-\frac{\Delta V}{V_0} \times 10^2$ (Calc.)	Obs.-Calc. $\times 10^4$	$-\frac{\Delta V}{V_0} \times 10^2$ (Calc.)	Obs.-Calc. $\times 10^4$
12000	10.432	3.1	11.205	1.7
11000	9.866	−0.2	10.608	0.0
10000	9.247	−3.0	9.951	−2.9
9000	8.565	−3.7	9.225	−2.5
8000	7.806	−2.6	8.414	−0.4
7000	6.953	1.4	7.498	3.7
6000	5.982	2.8	6.452	4.6
5000	4.861	6.4	5.238	−0.5
4000	3.546	2.0	3.808	−2.9
3000	1.970	−3.0	2.090	−3.4
2000	0.037	−3.7	− 0.026	2.6
1000	− 2.407	−3.5	− 2.708	2.6

The value of D may be estimated graphically as follows. It will be seen that the logarithm of the second derivative of y with respect to x is

$$\log \frac{d^2y}{dx^3} = \log (-CD^2) - Dx$$

or that the logarithm of $\frac{d^2y}{dx^2}$ is a linear function of x whose slope is $-D$. From a table of x as argument and y as entry we determined the second differences which corresponded to the second derivative. The logarithms of the second differences were plotted against x and the plot was approximately a straight line whose slope gave us an estimate of D. Using this value of D we were able to get tentative values of A, B, and C (A', B', and C') by substituting three of the observed values of x and y in Equation 3, and hence calculating values of y at all pressures. The differences between y obs. and y calc. (Δy) were plotted and a smooth deviation curve drawn. This curve was represented by the equation:

$$\Delta y = a + bx + c\,(1-e^{-Dx})$$

where D is the same as in the above calculation.

It may easily be shown that by adding a, b, and c to A', B', and C' an equation is obtained which gives the fairest representation of the data possible with an equation of this type.

The final equations were as follows:

$$y = -\ 9 + 482.2x\ + 5967\,(1-e^{-0.29x}) \qquad (3B)$$

$$y = -45 + 484.85x + 6890\,(1-e^{-0.27x}) \qquad (3C)$$

Calculations made with Equations 3B and 3C are tabulated in Table IV.

TABLE IV

REPRESENTATION OF RESULTS FOR TWO TYPES OF SOFT RUBBER BY AN EXPONENTIAL EQUATION

	Sample B		Sample C	
p	$-\frac{\Delta V}{V_0} \times 10^3$ (Calc.)	Obs.-Calc. $\times 10^4$	$-\frac{\Delta V}{V_0} \times 10^3$ (Calc.)	Obs.-Calc. $\times 10^4$
12000	10.452	1.1	11.231	−0.9
11000	9.859	0.5	10.602	0.6
10000	9.230	−1.3	9.929	−0.7
9000	8.549	−2.1	9.198	0.2
8000	7.804	−2.4	8.390	2.0
7000	6.969	−0.2	7.484	5.1
6000	6.016	−0.6	6.445	5.3
5000	4.905	2.0	5.235	−0.2
4000	3.581	−1.5	3.800	−2.1
3000	1.975	−3.5	2.070	−1.4
2000	− 0.009	0.9	− 0.045	4.5
1000	− 2.498	5.6	− 2.666	−1.6

Here, again, the magnitude of the residuals is greater than our estimated experimental error and undoubtedly Equation 3 does not represent the soft rubber results as well as the cubic equation represents those for the hard rubber. We would emphasize that the trend in the deviations of both the exponential and the hyperbolic equations, which is obvious from a study of Tables III and IV, should be taken as a warning that extrapolation with these equations is dangerous and that at best they are empirical interpolation formulas. On the other hand, we found that the course of $\frac{dy}{dx}$ as calculated from Equations 3B and 3C agreed very well with the course of the first differences of the observations from 1000 to 11,000 b., and, moreover, the value of $-\frac{\Delta V}{V_0}$ between 1 and 2000 b. calculated from the Equations 3B and 3C and corrected by the deviation curves agreed very well with our most reliable estimate obtained from a cubic passed through the points at 1000, 2000, and 3000 b.

Of all the equations fitted to the soft rubber results we prefer the exponential one. It represents the results as closely as does the hyperbola and is easier to handle.

For the hard rubber, smoothed reliable values of $-\frac{\Delta V}{V_0}$ reckoned from 2000 b. may be obtained at any pressure by application of Equation 1A, but as, up to the present, we have found no equation which represents the data to the order of the experimental error and even the course of the deviation curves is doubtful, we have no way of obtaining smoothed and accurate values of $-\frac{\Delta V}{V_0}$ for the samples of soft rubber. If it is desired to calculate this at intermediate pressures, Equations 3B or 3C may be used, which will give approximate values of $-\frac{\Delta V}{V_0}$ when used alone, and accurate ones when combined with the deviation curves.

In Fig. 1 we have plotted values of the relative decrease in volume, $-\frac{\Delta V}{V_0}$, reckoned from atmospheric pressure, against the pressure, for the three samples of rubber examined. These curves serve to illustrate the volume changes undergone by each type of rubber under hydrostatic pressure and, moreover, indicate the

consistency of our determinations. The points plotted in Fig. 1 are the observations taken from Table I to which has been added the average value of the volume change from 0 to 2000 b. estimated by all the equations and their deviation curves.

For Sample A, the hard rubber, the values of $-\frac{\Delta V}{V_0}$ reckoned from atmospheric pressure and corresponding values of the compressibility, β, are given by the equations

$$-\frac{\Delta V}{V_0} = 19.515 \times 10^{-6}p - 9.34 \times 10^{-10}p^2 + 2.121 \times 10^{-14}p^3$$

$$\beta = 19.515 \times 10^{-6} - 18.68 \times 10^{-10}p + 6.36 \times 10^{-14}p^2$$

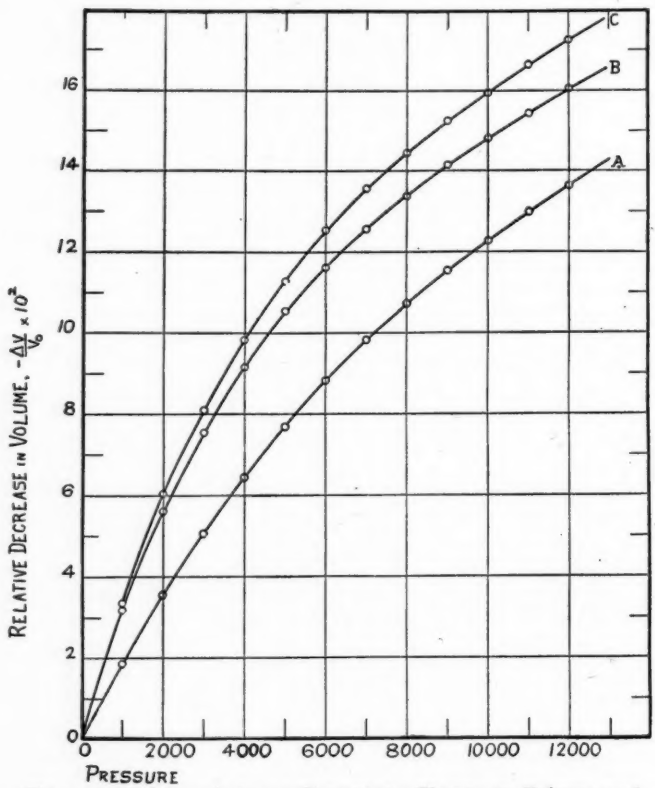

Figure 1—Relation between Percentage Change in Volume and Pressure for Three Samples of Rubber

where the pressure p is expressed in bars. These equations may be used directly to calculate the change in volume or the compressibility at any pressure.

Equations 4B and 4C give very close approximations to the compressibilities of Sample B and C, respectively.

$$\beta_B = \frac{dy}{dx} = 482.2 + 1730e^{-0.29x} \qquad (4B)$$

$$\beta = \frac{dy}{dx} = 484.5 + 1860e^{-0.27x} \qquad (4C)$$

Over the range from 2000 to 11,000 b. they are reliable, but if more accurate values are desired deviation curves may be constructed by plotting the figures in Columns 3 and 5 of Table IV against the pressure x, determining the slopes at the required pressures and adding them to the values of β calculated by 4B and 4C. As x is equal to $\frac{p-2000}{1000}$, where p is in b., we may convert Equations 4B and 4C to a form

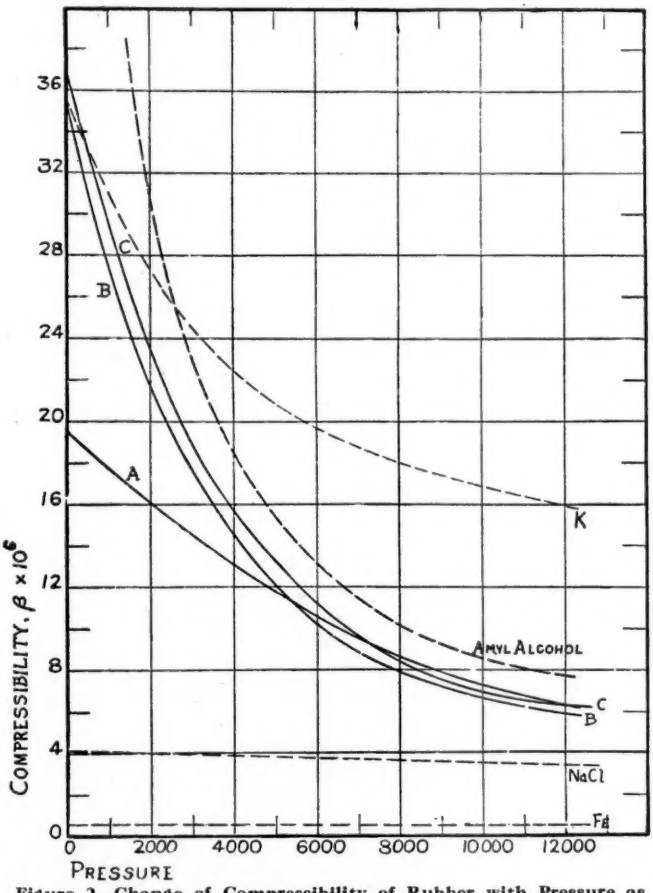

Figure 2—Change of Compressibility of Rubber with Pressure as Compared with That of Liquids and Solids

in which the pressure is given in b.

$$\beta_B = 4.822 \times 10^{-6} + 30.90 \times 10^{-6} e^{-0.00029p} \qquad (4'B)$$

$$\beta_C = 4.845 \times 10^{-6} + 31.92 \times 10^{-6} e^{-0.00027p} \qquad (4'C)$$

Discussion of Results.—The main results about the compressibility of rubber containing various amounts of sulfur are recorded graphically in Fig. 2, where they are compared with the compressibilities of a liquid, amyl alcohol;[8] of a highly

[8] P. W. Bridgman, *Proc. Am. Acad. Arts. Sci.*, **49**, 53 (1913).

compressible solid, potassium;[9] of a sodium chloride,[10] and of steel.[5] As might be expected, the compressibility-pressure curves for the two types of soft rubber are closely akin to the curve for amyl alcohol, the liquid, and show little in common with the curve for NaCl or even for potassium. It is true that the compressibility of potassium is the same as that of soft rubber at zero pressure, but the compressibility-pressure curves are radically different, resulting in the compressibility of rubber at 12,000 b. being approximately one-third of that of potassium. The compressibility-pressure curve of hard rubber (A) seems to be similar to that of potassium, being more like the curve of a compressible solid than that of a liquid.

Unavoidable differences in the volume of rubber washers used in the piston of the high-pressure apparatus result in the substitution of a small volume of pressure-transmitting liquid for rubber, or *vice versa*. We have just seen that the compressibility of rubber is not much less than that of organic liquids and so the magnitude of the correction introduced by the substitution of a few cubic millimeters of butyl ether for rubber is practically negligible.

It is interesting to note that while soft rubber, Sample B, is almost twice as compressible as hard rubber at atmospheric pressure, it is less compressible than the hard rubber at pressures above 5000 b. Undoubtedly the large amount of sulfur, 27 per cent. in the hard rubber, has a decided influence on its compressibility, lowering it at the lower pressures and keeping the value large at the high pressures. In fact, Curve A might well be regarded as composed of two curves, the first similar to Curve B and the second a straight line cutting the y-axis at 13.1 and of slightly negative slope. The compressibility of sulfur is 13.1 at 1 mb.[11] and it probably exhibits the normal diminution with pressure. Figure 1 shows that if the volume of a piece of hard rubber is 100 cc. at atmospheric pressure, its volume at 12,000 b. is only 85.4 cc. and that under a similar pressure change the volume of a piece of soft rubber containing 10 per cent. of sulfur would decrease from 100 cc. to 82.8 cc. These figures emphasize in a striking way the very large changes in volume which are produced when a solid like rubber is subjected to large hydrostatic pressure.

[9] P. W. Bridgman, *Proc. Am. Acad. Arts. Sci.*, **58**, 204 (1923).
[10] Adams, Williamson and Johnston, *Op. cit.*
[11] T. W. Richards, *Jour. Am. Chem. Soc.*, **37**, 1646 (1915).

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Studies in the Oxidation of Rubber Mixings

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In a former communication (*Trans. Inst. Rubber Industry*, **4**, 493 (1929)) some results were presented of studies on the changes of rubber samples oxidized to an intense degree. For that investigation the oxidation temperature used was 70° C. (Geer Oven), while in the present paper results are given of experiments made at 100° C. and their relation to the results at the lower temperature are discussed. The experimental procedure was similar to that previously used, the preliminary

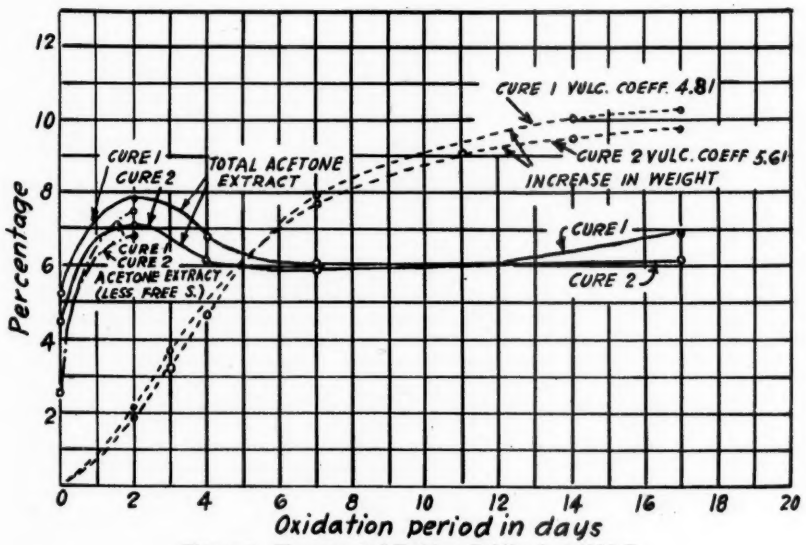

Figure 1—Unextracted Rubber Oxidized at 100° C.

stage being the sheeting out of small portions of the samples by passing them through the tightly closed cold rolls of a laboratory mill. The weighed samples were then suspended by strings in an ordinary steam oven fitted with an air inlet near the bottom and an outlet at the top. The progress of oxidation of each sample was noted from time to time by (*a*) determining the increase in weight, and (*b*) removing and estimating the amount of resinous matter present by extraction with acetone for 24 hours. In some instances the acetone extraction was preceded by an extraction with chloroform.

A. Rubber Sulfur Mixings

(*1*) *Unextracted Rubber.*—The curves in Fig. 1 show the effect of oxidation on two samples of a rubber-sulfur mixing (100:8) of differing vulcanization coefficients, both samples being shown on test to be well cured.

The effect of the higher temperature was to bring about very rapid oxidation, which in the early stages was four or five times as rapid as the oxidation of similar samples at 70° C. The increases in weight at the two temperatures tended to be of the same order after prolonged oxidation, but the oxidation at 100° C. differed from that at 70° C. in that after strong oxidation the sample with the lower degree of vulcanization yielded a higher increase in weight. The probable reason for this is the greater loss of volatile matter by the higher cured sample. It is seen that in the early stages of oxidation there was a rapid formation of acetone extract, but this equally rapidly was partly converted into insoluble matter resulting in a fall in the amount of extract. This effect, believed to be essentially due to polymeriza-

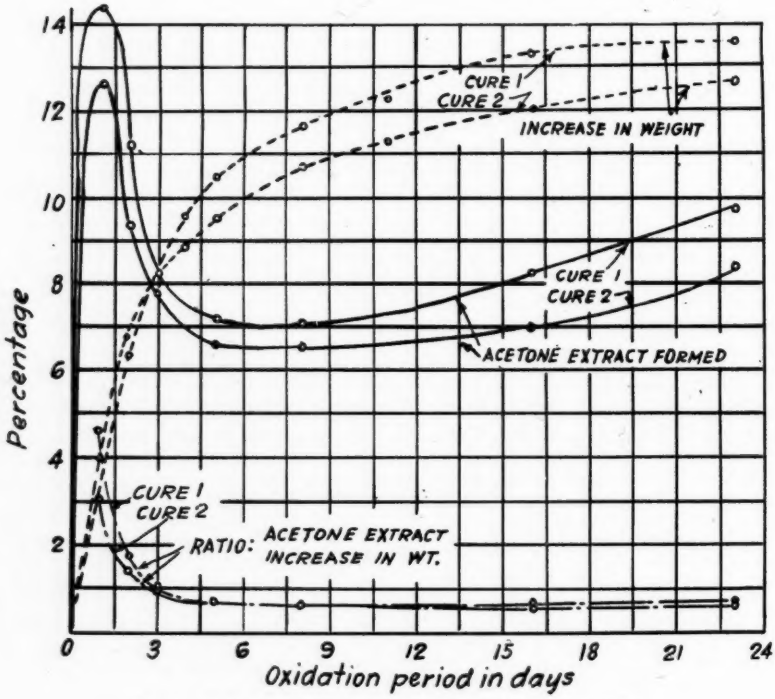

Figure 2—Acetone-Extracted Rubber Oxidized at 100° C.

tion of the extract, was shown much more definitely at 100° C. than at 70° C. After the first rapid changes the amount of extract remained constant over a long period of heating.

It will be noted that the oxidation curves at 100° C. are close together, indicating that at the higher temperature the effect of cure was less pronounced.

(*2*) *Acetone-Extracted Rubber.*—The samples which were used above were submitted to acetone extraction and then oxidized at 100° C. Figure 2 shows the results obtained. The oxidation was very rapid, in this case also being about four times as rapid as for similar samples at 70° C.

The final increases in weight tended to be rather less than for similar rubber-sulfur mixings oxidized at 70° C. and as with the oxidation of the unextracted

samples at 100° C. the increase in weight on prolonged heating was higher for the lesser cured sample.

The production of acetone-soluble matter was at first very large, but polymerization soon took place and the extracts obtained during the fairly constant period were much lower than those usually obtained at 70° C. It is believed that the ratio: $\frac{\text{acetone extract}}{\text{increase in weight}}$ indicates to a certain degree the extent to which the absorbed oxygen passes into acetone-soluble matter. On comparing the ratios $\frac{\text{acetone extract}}{\text{increase in weight}}$ at 70° C. and 100° C. it was seen that these were of the same order in the early stages but after prolonged oxidation the figures were much lower

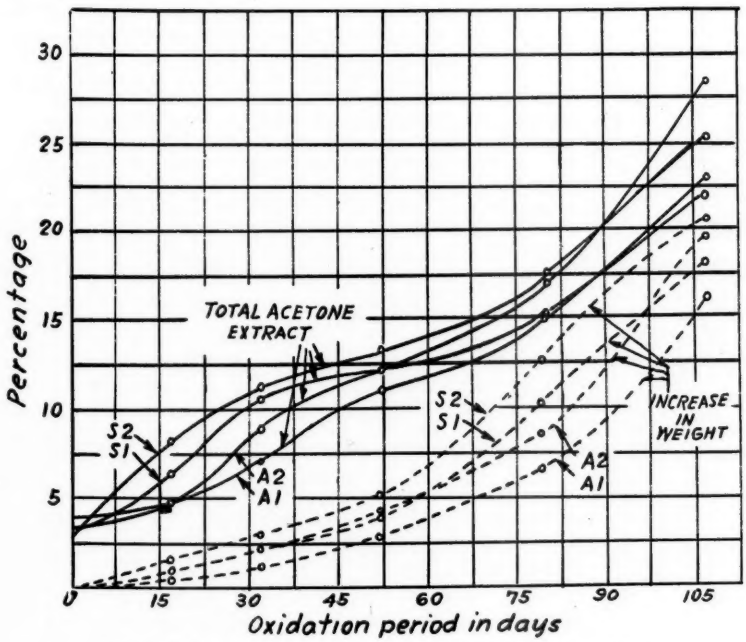

Figure 3—Accelerator-Antioxidant Mixing Oxidized at 70° C.

	S	A		S	A		S	A
Rubber	100	100	Sulfur	3	3	Zinc Oxide	3	3
D.P.G.	3/4	3/4	Agerite R.	–	1			

Cure 1—5 mins. rise, 40 mins. at 40 lbs. Cure 2—5 mins. rise, 60 mins. at 40 lbs.

at 100° C. It is believed that the explanation of this effect is that polymerization of the acetone extract to an insoluble form is a relatively slow process and that in the early stages of oxidation at 100° the production of acetone extract was so rapid that there was insufficient time for much polymerization to take place. However, after longer oxidation the greater tendency to polymerization at the higher temperature was made evident.

As was noted in the case of the unextracted samples the curves at 100° C. are close together indicating that the higher temperature had an evening-up influence. This was further shown by the fact that at 100° C. the difference between the results

obtained from the unextracted and acetone-extracted samples was much less marked than at 70° C. By comparison of the curves in Figs. 1 and 2 it will be seen that after about five days' oxidation, apart from the curves of the acetone-extracted samples giving higher figures the increase in weight and acetone-extract curves for the unextracted and extracted samples follow very similar courses.

(3) *Further Aging of the Acetone Extracts.*—The acetone extracts formed on aging at 100° C. could be largely converted into an acetone-insoluble form by further heating. As was the case at 70° C., the heating generally brought about an increase in weight at the same time, the amount of this increase depending on the extent to which the extract was already oxidized.

B. Accelerated Mixings

(1) *Containing a Medium Accelerator (Diphenylguanidine) and an Antioxidant (Agerite Resin).*—Figures 3 and 4 show curves for an accelerated mixing (with and

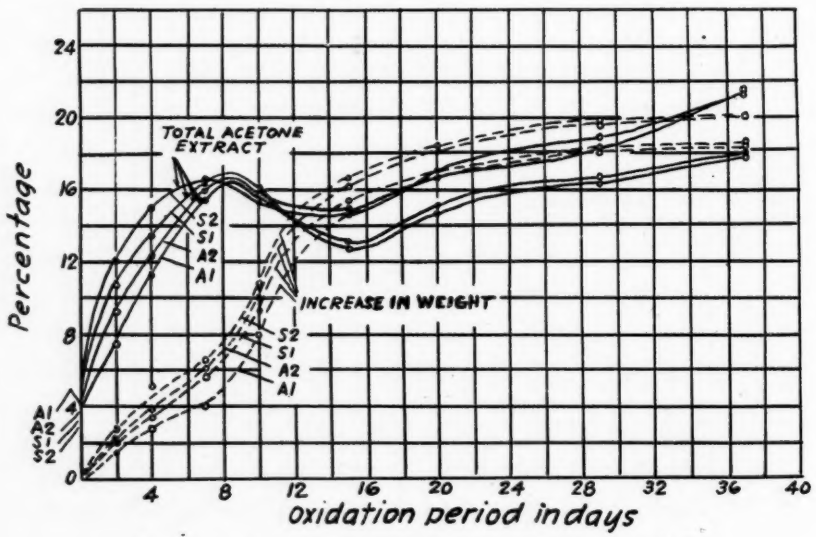

Figure 4—Accelerator-Antioxidant Mixing Oxidized at 100° C.

	S	A		S	A		S	A
Rubber	100	100	Sulfur	3	3	Zinc Oxide	3	3
D.P.G.	¾	¾	Agerite R.	–	1			

without an antioxidant) submitted to oxidation at 70° C. and 100° C., respectively. The mixing was chosen as a flat curing one as regards tensile properties and no cure adjustment was made for the additional antioxidant added.

Relative to oxidation at 70° C. the higher temperature increased enormously the rate of oxidation (some 15 times in the early stages) and brought about types of entirely different acetone-extract curves.

The results showed that the effect of the antioxidant was to give a definitely smaller increase in weight, the figures for the antioxidant mixing being lower than those of the corresponding standard mixing. It is seen that the longer cured antioxidant mixing followed approximately the same course as the shorter cured standard mixing but a comparison of the position of the increase in weight curves at

70° C. and 100° C. indicates that the effect of the antioxidant was more pronounced at the lower temperature.

By comparing the increases in weight, after long aging, given in Figs. 1 and 4, it will be seen that the accelerated mixing gave much higher results than did the rubber-sulfur mixing. It is evident, therefore, that if the oxidation is prolonged, the increase in weight, by itself, is not a suitable criterion for comparing the oxidation of different types of mixings.

At 100° C. the acetone-extract curves (Fig. 4) mounted fairly rapidly in the early stages of oxidation to figures much higher than those given by the rubber-sulfur mixings (Fig. 1). The first production of acetone extract was followed by a polymerization, the longer cured samples then giving higher extracts than the shorter cured sample. Comparison with Fig. 3 also shows that after strong oxidation at 70° the higher cured samples gave the higher extracts. Further, after long oxidation, both at 70° and 100° the antioxidant samples tended to produce slightly higher extracts than the corresponding standard samples.

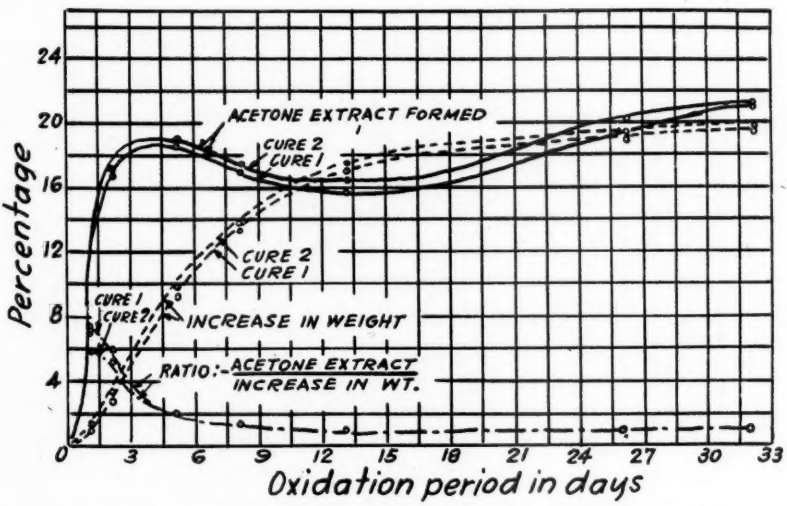

Figure 5—Accelerated Mixing (Acetone-Extracted) Oxidized at 100° C.

Rubber, 100. Sulfur, 3. Zinc Oxide, 3. D.P.G., 3/4.

(2) *Containing a Medium Accelerator (Diphenylguanidine) and Rubber, Acetone-Extracted before Oxidation.*—The standard mixing samples used for the previous series were, after acetone extraction, oxidized at 100° C. and yielded the results given in Fig. 5.

The curves show that the ultimate increases in weight were of the same order as for the unextracted rubber but acetone extraction led to an evening-up of the figures, the curves for the two cures showing only small differences.

The acetone-extract curves were very similar in form to those of the unextracted rubbers, but they reached higher maxima and stood at higher figures during the fairly flat parts of the curves. Comparison of Figs. 2 and 5 shows that the accelerated samples yielded much higher acetone extracts than did the rubber-sulfur samples. This was similar to the effect observed during oxidation at 70° C.

It will be observed that, as in the case of the rubber-sulfur samples (Fig. 2),

the figures for the ratios $\frac{\text{acetone extract}}{\text{increase in weight}}$ were high in the early stages but were very low when oxidation was prolonged.

(3) *Containing a Semi-Ultra Accelerator (Captax) and Unextracted Rubber.*—Figure 6 shows the results obtained on oxidizing two samples containing Captax at 100°. During the early stages of oxidation (say, the first four days) the cure 1 sample was definitely slower oxidizing than cure 2 sample, but after 8 days or more, the results for the two samples were very similar.

A consideration of the increase in weight curves shows that, although in a general way they have a similar form to the curves given by the samples which have previously been discussed, the Captax mixing provides a contrast by giving a sudden rapid increase in weight after about four days. A comparison of Figs. 3 and 6 shows that the samples containing diphenylguanidine did not show this rapid rise but they increased in weight fairly steadily. Thus, while during the first few days'

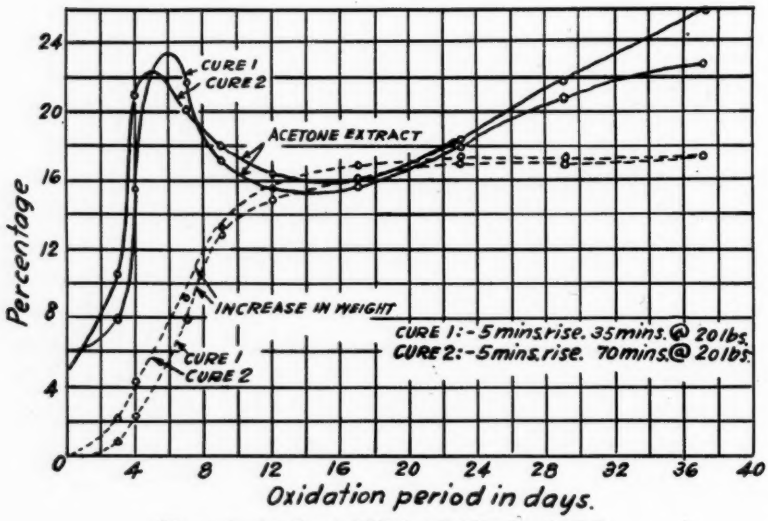

Figure 6—Accelerated Mixing Oxidized at 100° C.

Rubber, 100. Sulfur, 3. Zinc Oxide, 3. Stearic Acid, 2. Captax, 0.8.

oxidation the Captax samples gave considerably lower increases in weight than the samples containing diphenylguanidine, after seven days the Captax samples had definitely higher figures. It will be noted, however, that the final increases in weight reached by the diphenylguanidine samples were higher than those of the Captax samples.

The acetone extracts formed on oxidizing the Captax mixing were much higher throughout than those for the diphenylguanidine mix, this difference being clearly seen in the case of the maximum acetone extracts. Figure 6 shows that although the cure 1 sample reached a higher maximum acetone extract than the cure 2 sample, the latter gave slightly higher figures during the flat part of the curves. This result is similar to that recorded in the case of the diphenylguanidine mixing.

(4) *Containing a Semi-Ultra Accelerator (Captax) and Rubber Acetone-Extracted before Oxidation.*—The Captax mixing was extracted with acetone and then oxidized at 100° C. Figure 7 shows the course of the results.

A comparison of these results with those of the diphenylguanidine mixing (Fig. 5) shows that, whereas the Captax mixing was more resistant to oxidation in the early stages, after about eight days' oxidation the increases in weight were practically equal. The ultimate increases in weight were almost the same for the two mixings and two cures. The acetone extracts rose to very high figures, being higher than those given by the diphenylguanidine mixing. This large formation of acetone extract was followed by a rapid polymerization with the result that after eight days the Captax samples gave lower extracts than the diphenylguanidine mixes and the fairly flat parts of the curves stood at slightly lower levels.

The figures for the ratios $\frac{\text{acetone extract}}{\text{increase in weight}}$ were very high in the early stages, indicating that the production of insoluble oxidation products was very small, but the figures fell rapidly to values similar to those given by the diphenylguanidine mixing.

(5) *Summary of Results.*—The chief results of the experiments on oxidation at 100° C. may be summarized as follows:

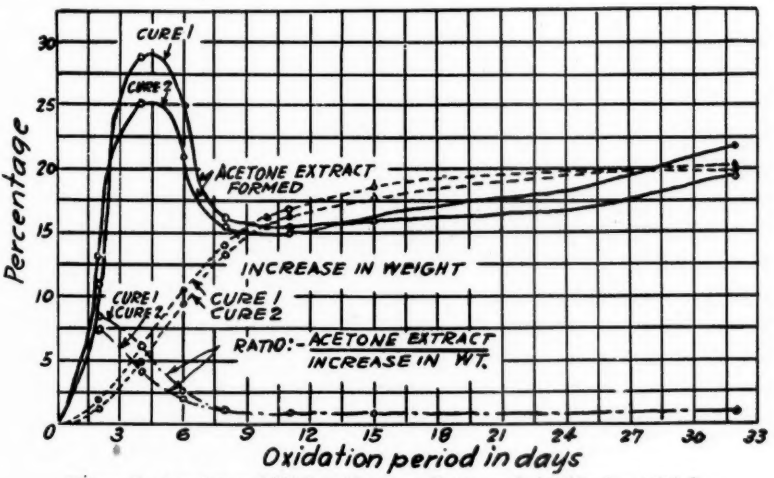

Figure 7—Accelerated Mixing (Acetone-Extracted) Oxidized at 100° C.

Rubber, 100. Sulfur, 3. Zinc Oxide, 3. Stearic Acid, 2. Captax, 0.8

(1) Oxidation at 100° C. is very rapid but the ultimate increases in weight do not differ greatly from those for the same samples oxidized at 70° C.

(2) There is a marked evening-up of the rates of oxidation, and the effect of acetone extraction prior to oxidation is much less noticeable compared with its effect at 70° C.

(3) All the acetone-extract curves show definite maxima due to the rapid change of the acetone extracts into an insoluble form. This change of the extract is more complete at 100° C. than at 70° C. resulting in lower extracts being obtained.

C. A Comparison of the Oxidation of Rubbers Cured with Different Accelerators

It has been shown earlier that different accelerators produce rubbers differing considerably on oxidation and, in order to study the differences more closely,

mixings were made with a range of widely different accelerators and submitted to oxidation. The mixings taken were considered typical of the accelerators concerned and the samples were given a range of three cures varying from slight undercure to a full cure. For comparison a rubber-sulfur-zinc oxide mixing was put through the same procedure as the accelerated mixings.

The results obtained are entered in Table I, which also gives figures for the chloroform extracts, determinations of which were made for this series. It should be noted that in this table the "acetone extract formed" is entered for purposes of simplification. This was obtained by deducting the amount of "acetone extract less free sulfur" present in the unoxidized samples from the amount present after oxidizing. For purposes of reference the tensile properties of the unoxidized samples are also given.

The oxidation of a series of samples was always carried out simultaneously, this being done in order to eliminate experimental differences due to repetition, thickness of sheet variations, oven temperature differences, etc.

TABLE I

Mixings	Rubber	Sulfur	Zinc Oxide	Accelerator
Rubber-sulfur-zinc oxide	100	8	5	..
L. C. Magnesia	100	6	5	1
Hexamine	100	5	5	1
Tuads	100	3	5	1/4 + 1/8 litharge
D. P. G.	100	3 1/2	5	3/4
808	100	3	5	1
XA (Ethylidene-aniline type)	100	3 1/2	5	1
Vulcanol	100	4	5	1
Captax	100	3	5	1/2

In the Captax and Tuads mixings 1 part of stearic acid was added.

	Cure	Elongation Per Cent. at 0.5 Kg./Mm.²	Elongation Per Cent. at Break	Tensile Strength, Kg./Mm.²
Rubber-sulfur-zinc oxide mix.	5–120–50	755	920	1.28
	5–140–50	711	895	1.48
	5–160–50	660	870	1.57
L. C. M. Mix.	5–90–50	612	840	1.58
	5–110–50	578	833	1.78
	5–130–50	551	820	1.79
Hexamine	5–40–50	619	780	1.27
	5–60–50	558	725	1.46
	5–80–50	518	730	1.80
Tuads	5–10–30	595	795	1.67
	5–20–30	543	728	1.71
	5–30–30	539	725	1.92
D. P. G.	5–30–40	581	770	1.62
	5–50–40	520	715	1.79
	5–70–40	502	705	1.85
808	5–25–25	526	735	2.02
	5–35–25	481	710	2.22
	5–45–25	455	680	2.33
XA	5–15–25	633	800	1.28
	5–25–35	603	770	1.36
	5–35–35	580	760	1.49
Vulcanol	5–20–20	596	785	1.51
	5–30–20	548	760	1.89
	5–40–20	529	725	1.81
Captax	5–25–20	634	820	1.52
	5–40–20	575	775	1.70
	5–55–20	564	765	1.74

5–120–50 indicates 5 minutes' rise to 50 lbs., and 120 minutes' cure at 50 lbs. and so on accordingly.

Oxidation Period in Days	Cure 1			Cure 2			Cure 3		
	3	7	14	3	7	14	3	7	14
				Rubber-Sulfur-Zinc Oxide Mix.					
A	3.99	3.46	3.58	4.16	3.96	3.36	4.33	3.74	4.22
B	2.83	7.29	9.58	3.50	7.85	10.01	4.61	7.84	11.10
C	1.31	0.35	0.35	0.84	0.12	0.40	0.56	0.11	0.37
A/B	1.41	0.47	0.37	1.19	0.50	0.34	0.94	0.48	0.38
				L. C. M. Mix.					
A	6.20	4.57	4.44	6.29	5.15	4.10	6.61	4.71	4.28
B	4.46	9.16	11.75	5.67	10.43	12.13	6.43	9.46	12.35
C	1.34	0.39	0.25	0.84	0.09	0.33	0.50	0.06	0.31
A/B	1.39	0.60	0.38	1.11	0.50	0.34	1.02	0.50	0.35
				Hexamine					
A	4.59	7.61	8.50	6.84	9.30	8.09	7.56	8.55	8.33
B	0.84	3.50	8.06	2.28	5.97	12.35	4.36	8.24	14.35
C	9.60	6.40	0.91	5.40	1.94	0.53	2.91	0.61	0.37
A/B	5.47	2.18	1.05	3.00	1.56	0.65	1.74	1.04	0.58
				Tuads					
A	11.70	15.21	10.38	15.10	13.71	9.76	14.90	13.67	9.83
B	1.72	6.67	11.65	2.58	7.59	12.95	3.53	7.84	14.43
C	12.90	1.99	0.56	7.55	1.41	0.43	5.99	1.22	0.52
A/B	6.80	2.28	0.89	5.86	1.81	0.75	4.22	1.74	0.68
				D. P. G.					
A	5.96	9.90	9.23	7.23	11.87	9.00	16.89	10.42	10.52
B	1.26	4.45	10.25	2.39	6.54	12.45	4.12	7.78	15.20
C	12.05	5.55	0.62	7.62	2.15	0.52	4.60	1.07	0.45
A/B	4.23	2.22	0.90	3.03	1.82	0.72	4.10	1.34	0.68
				808					
A	8.73	11.72	10.22	9.50	11.38	9.70	10.00	11.76	10.83
B	1.06	4.60	10.85	1.54	5.93	11.30	2.63	6.56	14.96
C	10.60	5.20	0.65	6.40	2.10	0.46	5.15	1.60	0.53
A/B	8.24	2.55	0.94	6.16	1.92	0.86	3.81	1.79	0.73
				XA					
A	4.04	10.39	11.97	6.54	11.31	10.77	8.09	9.52	10.64
B	0.11	2.31	6.81	0.72	3.63	8.60	1.48	3.73	10.00
C	17.30	12.55	1.69	11.30	5.50	0.82	8.85	5.83	0.60
A/B	36.7	4.46	1.75	9.09	3.12	1.25	5.47	2.55	1.06
				Vulcanol					
A	3.43	9.53	8.65	5.55	9.90	9.19	8.05	8.89	9.68
B	−0.31	2.11	7.65	0.54	2.33	8.35	0.54	2.91	9.46
C	14.15	6.70	0.85	12.35	5.69	0.84	8.90	3.85	0.53
A/B	...	4.52	1.13	...	4.24	1.10	14.88	3.05	1.02
				Captax					
A	4.64	17.21	10.14	6.57	14.13	10.77	9.96	7.26	11.34
B	1.00	6.86	13.38	1.55	7.14	13.45	2.12	7.38	14.07
C	3.04	1.47	0.42	3.60	1.02	0.53	5.40	1.47	0.66
A/B	4.64	2.51	0.76	4.24	1.98	0.79	4.70	0.98	0.77

A Acetone extract formed per cent.
B Weight increase per cent.
C Total chloroform extract per cent.
A/B Ratio of acetone extract formed to increase in weight.

A consideration of the results in a general manner shows that the weight steadily increased during the period of aging and for the same oxidation period the longer the cure the higher the increase in weight.

The amount of chloroform extract increased rapidly on oxidation but again decreased when the time was lengthened. For the same oxidation period the amount of chloroform extract decreased with the time of cure.

With increasing oxidation periods the amount of acetone extract formed increased, or increased and subsequently decreased, according to the particular accelerator used. In most cases the amount of extract formed increased with the degree of cure, but in some cases it increased and then subsequently decreased, depending on the accelerator taken. The ratio $\frac{\text{acetone extract formed}}{\text{increase in weight}}$ decreased with the time of oxidation and also with the degree of cure.

The above generalizations are largely merely confirmatory of previous experience and it is further evident that after prolonged oxidation the increase in weight alone is not a safe criterion as to the relative oxidizing tendencies of different mixings.

In considering the relative superiority of the different mixings, isolated figures are apt to be misleading, and it is necessary, therefore, to consider the results as a whole, that is for all three cures and for all the different aging periods.

On a weight increase basis the mixings appear to be in the following order: Vulcanol, XA, 808, Captax, diphenylguanidine, Tuads, Hexamine, rubber-sulfur-zinc oxide, Light Carbonate of Magnesia. The weight increase alone may be misleading owing to volatile losses of sulfur, accelerator, etc., and it will be noted that the Vulcanol mixing decreased in weight slightly in the early stages of oxidation.

The hexamine figures are influenced by the volatility of this accelerator, with the result that some appear abnormally low. The Captax mixing would have ranked higher but for the tendency it showed of a small increase in weight in the early stages of oxidation and then a sudden rapid increase on further oxidation (cf. supra).

Taking the chloroform extract as a criterion, on the assumption that a high chloroform extract indicates a small tendency to oxidation, the mixings appear as follows: XA, Vulcanol, diphenylguanidine, 808, Tuads, Captax, L. C. M., rubber-sulfur-zinc oxide.

The ratio $\frac{\text{acetone extract}}{\text{increase in weight}}$ is naturally influenced by loss of volatile matter, but nevertheless, it is believed that these figures can be satisfactorily used for indicating the tendency of the accelerator to cause the rubber to remain soft or to become brittle. On this basis the mixings appear in the following order: Vulcanol, XA, 808, Tuads, Captax, diphenylguanidine, Hexamine, L.C.M., rubber-sulfur-zinc oxide.

In one case a figure which appears to be abnormally high is given by the Hexamine mix. This is probably caused by the low increase in weight due, as already mentioned, to volatility of the accelerator.

It is thus seen that by whatever criterion the tendency to oxidation is judged, Vulcanol, XA (Ethylidene-aniline type) and 808 always stood high. These accelerators are all of the aldehyde-amine class and it is concluded, therefore, that this type of accelerator is particularly suitable for use under conditions of heat oxidation (cf. Dinsmore and Vogt, *Trans. Inst. Rubber Industry*, **4**, 98 (1928)). Captax was relatively less satisfactory under these conditions than in oxidation at lower temperatures, and rubber-sulfur or L. C. M. mixings were greatly inferior to the mixings containing any of the organic accelerators which were tested.

D. Effect of Different Fillers on the Oxidation Changes

(*1*) *Mineral Fillers.*—The effect of different mineral fillers on the oxidation of a standard mixing was studied, four different fillers (10 volumes per cent.) being introduced into the mixing: rubber 100, sulfur 3, zinc oxide 3, Captax 0.8, stearic acid 2. This mixing was chosen as being flat curing in tensile properties and the

same mixing samples were used for permeability determinations (Davey and Ohya, *Trans. Inst. Rubber Industry*, **5**, 27 (1929)). It was found, however, that it did not follow from flatness of tensile properties that differently cured samples oxidized similarly (cf. Dinsmore and Vogt, *loc. cit.*, 95) and experimental series were made at two different cures.

The extraction figures were calculated on the percentage of rubber in the mixing, this percentage varying with the specific gravity of the filler concerned. The fillers studied were: carbon black, zinc oxide, Dixie clay and whiting.

The filler mixings gave greater increases in weight than the standard mixing. Carbon black was an exception, this result being almost certainly due to its marked retardation of cure. Even after allowing for this cure retardation, on account of which it gave particularly good results, the mixings containing carbon black oxidized less than those containing the other fillers (with the possible exception of zinc oxide). Zinc oxide maintained high figures for the chloroform extract, acetone extract, and the ratio: $\frac{\text{acetone extract}}{\text{increase in weight}}$ over a long oxidation period. This filler, therefore, appears to possess very good properties from oxidation standpoints. Dixie clay did not give very good results and whiting gave the poorest of all.

The general results of these experiments (see Table II) indicate, therefore, that the finer the filler the more suitable it is for use under conditions of high temperatures. There appears to be a fairly direct relation between the permeability of a rubber mixing and its tendency to oxidation at high temperatures (Davey and Ohya, *loc. cit.*). Coarse fillers should, therefore, be avoided in mixings to be used at high temperatures as they will cause the rubber to oxidize and become brittle sooner. There are, however, specific effects due to each filler and zinc oxide appears particularly suitable where heat oxidation is concerned. The good effects with this filler are probably due to its basic properties by virtue of which it tends to prevent the change of acetone extract to insoluble matter.

TABLE II

EFFECT OF DIFFERENT MINERAL FILLERS ON THE OXIDATION AT 100° C.

Rubber 100 Sulfur 3 Zinc Oxide 3 Captax 0.8 Stearic Acid 2

10 vols.-per cent. of filler on rubber added

Cure 1: 5 min. rise, 40 min. at 20 lb.
Cure 2: 5 min. rise, 75 min. at 20 lb.

CURE 1

		Unoxidized	Oxidized 7 Days	Oxidized 14 Days
Standard:				
A	Total acetone extract	5.96	17.95	14.90
B	Free sulfur	1.18	0.24	0.14
C	Acetone extract, less free S (on rubber)	5.21	19.20	16.10
D	Chloroform extract (on rubber)	..	2.76	0.54
E	Increase in weight (on rubber)	..	5.13	14.50
F	Ratio: $\frac{\text{acetone extract}}{\text{increase in weight}}$	..	3.74	1.11
Carbon black:				
A	Total acetone extract	5.88	17.60	10.90
B	Free sulfur	1.76	0.15	0.08
C	Acetone extract, less free S (on rubber)	5.29	22.30	13.85
D	Chloroform extract (on rubber)	..	4.40	0.52
E	Increase in weight (on rubber)	..	2.83	11.56
F	Ratio: $\frac{\text{acetone extract}}{\text{increase in weight}}$	..	7.90	1.19

		Unoxidized	Oxidized 7 days	Oxidized 14 days
Zinc Oxide:				
A	Total acetone extract	3.94	17.60	16.00
B	Free sulfur	0.59	0.15	0.10
C	Acetone extract, less free S (on rubber)	5.65	29.60	26.80
D	Chloroform extract (on rubber)	..	3.80	1.16
E	Increase in weight (on rubber)	..	5.53	16.80
F	Ratio: $\frac{\text{acetone extract}}{\text{increase in weight}}$	..	5.34	1.59
Dixie Clay:				
A	Total acetone extract	4.93	20.30	11.80
B	Free sulfur	1.11	0.20	0.10
C	Acetone extract, less free S (on rubber)	5.23	27.60	16.10
D	Chloroform extract (on rubber)	..	1.63	0.46
E	Increase in weight (on rubber)	..	6.60	15.30
F	Ratio: $\frac{\text{acetone extract}}{\text{increase in weight}}$	..	4.14	1.05
Whiting:				
A	Total acetone extract	4.79	18.90	12.85
B	Free sulfur	0.73	0.20	0.12
C	Acetone extract, less free S (on rubber)	5.60	25.70	17.60
D	Chloroform extract (on rubber)	..	1.34	0.69
E	Increase in weight (on rubber)	..	7.55	16.30
F	Ratio: $\frac{\text{acetone extract}}{\text{increase in weight}}$	..	3.38	1.08

CURE 2

		Unoxidized	Oxidized $3\frac{1}{2}$ Days	Oxidized 7 Days
Standard:				
A	Total acetone extract	4.85	14.90	18.50
B	Free sulfur	0.72	0.27	0.26
C	Acetone extract, less free S (on rubber)	4.50	16.00	19.90
D	Chloroform extract (on rubber)	1.12	2.14	1.15
E	Increase in weight (on rubber)	..	3.21	9.05
F	Ratio: $\frac{\text{acetone extract}}{\text{increase in weight}}$	..	4.99	2.20
Carbon Black:				
A	Total acetone extract	4.87	20.20	17.10
B	Free sulfur	1.06	0.23	0.15
C	Acetone extract, less free S (on rubber)	4.87	25.60	21.82
D	Chloroform extract (on rubber)	1.18	5.28	1.43
E	Increase in weight (on rubber)	..	2.88	6.73
F	Ratio: $\frac{\text{acetone extract}}{\text{increase in weight}}$	..	8.88	3.25
Zinc Oxide:		Unoxidized	Oxidized 7 Days	Oxidized 14 Days
A	Total acetone extract	3.30	16.20	17.20
B	Free sulfur	0.40	0.20	0.19
C	Acetone extract, less free S (on rubber)	4.90	27.20	28.90
D	Chloroform extract (on rubber)	0.50	4.35	2.38
E	Increase in weight (on rubber)	..	3.20	7.68
F	Ratio: $\frac{\text{acetone extract}}{\text{increase in weight}}$	..	8.52	3.68
Dixie Clay:				
A	Total acetone extract	4.37	16.01	15.75
B	Free sulfur	0.73	0.24	0.19
C	Acetone extract, less free S (on rubber)	4.99	21.70	21.40
D	Chloroform extract (on rubber)	0.74	5.28	1.13
E	Increase in weight (on rubber)	..	3.05	11.00
F	Ratio: $\frac{\text{acetone extract}}{\text{increase in weight}}$	..	7.13	1.95
Whiting:				
A	Total acetone extract	4.10	18.20	15.30
B	Free sulfur	0.51	0.24	0.16

C	Acetone extract, less free S (on rubber)	4.95	24.80	20.90
D	Chloroform extract (on rubber)	1.05	3.06	1.15
E	Increase in weight (on rubber)	..	3.98	10.70
F	Ratio: $\frac{\text{acetone extract}}{\text{increast in weight}}$	..	6.23	1.96

(*2*) *Stearic Acid.*—In view of the results obtained by the use of zinc oxide, the effect noticed being due presumably to its basic properties, it was decided to study the effect of an acidic substance. Stearic acid was taken because of its very wide use, and in order to eliminate complications the study was made in a rubber-sulfur mixing.

Mixings:	A.	Rubber	100	Sulfur	8		
	B.	Rubber	100	Sulfur	8	Stearic Acid	3
Cures:	(1)	5–80–50	(2)	5–100–50	(3)	5–120–50	

The presence of stearic acid tended on oxidation to produce slightly lower weight increases, slightly higher chloroform extracts, but definitely lower acetone extracts. The ratios $\frac{\text{acetone extract}}{\text{increase in weight}}$ were also lower and it is concluded, therefore, that the change of acetone extract to acetone insoluble matter is assisted by the presence of the acid.

(*3*) *White Substitute.*—In view of the fact that white substitute was included in certain published mixings recommended for airbags it was decided to ascertain if any substantiating evidence could be found for the use of this material.

Mixing:	A.	Rubber	100	Sulfur	8			
	B.	Rubber	100	Sulfur	8	White Substitute		15
Cures:	A.	(1) 5–100–50		(2) 5–120–50		(3) 5–140–50		
	B.	(1) 5–180–50		(2) 5–200–50		(3) 5–220–50		

The white substitute retarded the cure considerably and produced a "dead" rubber apparently not greatly influenced by the time of cure given.

The increases in weight of the white substitute samples were much lower than those of the standard samples. The chloroform extracts of the white substitute samples were higher than the standard samples both for the unoxidized and oxidized rubbers and the acetone extract ratios were also higher in the substitute series than in the standard series.

It was concluded, therefore, that even if considerably longer cure times are given the use of white substitute in a mixing is beneficial in reducing the tendency to oxidation. It has to be remembered, however, that the use of this filler may produce a "deadness" which may be otherwise undesirable.

E. Study of the Effect of Different Antioxidants

The effect on the course of oxidation at 100° C. of a number of well-known antioxidants has also been studied along the lines indicated. The efficacy of antioxidants is influenced by the mixing used, some for example being more effective in an acidic medium, others in a basic one (cf., however, *India Rubber J.*, **75,** 585, 824 (1928)). Further, some of them have an effect on the cure, so that altogether their full study is very complicated and involves a very large investigation covering a range of mixing and several different cures. (Garner, *India Rubber J.*, **77,** 31 (1929).)

At the present time such investigation is not yet completed but it is hoped to publish the full results later.

The studies, so far made, have disclosed, however, that the typical organic antioxidants act essentially during the oxidation change of the chloroform extract to acetone extract and that they do not greatly influence the change of acetone extract to insoluble matter.

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The Constitution of Rubber According to Its Swelling in Liquids

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I. Introduction

As a colloidal substance rubber has been the object of numerous and frequent controversies over its constitution in the solid state, in the swollen state and in the dissolved state. In fact, the swelling is interpreted in very different ways according to the hypothesis adopted in regard to its constitution in the solid state.

We shall not repeat the various concepts relative to the state of a colloidal substance outside of any solvent; the different interpretations of the phenomena observed are known to all. In the present memoir we propose to present new arguments in favor of the hypothesis by which the hydrocarbon, of which the chief part of unvulcanized rubber is composed, is formed of an intimate mixture of a series of isoprene polymers which differ among themselves in the degree of polymerization; the average value of the degree of actual polymerization being dependent on the temperature and the previous history of the sample under consideration. The hydrocarbon contains some parts of relatively high polymerization formed of long molecular chains and parts of shorter chains. In the series of polymers, which is probably continuous, two types are to be distinguished, which differ in their degree of diffusibility in "solvents" of rubber. Feuchter[1] has shown that these two types of components can be separated, and our experiments in collaboration with Fleurent[2] have shown the variability of the relative quantities of these two components under different conditions. Finally, as a result of the work by Hauser[3] on x-ray diagrams of rubber and the conclusions drawn from it, Hauser and the writer[4] have been able to verify that results obtained from essentially different methods of work lead to the same concept on the constitution of rubber under the condition that the more diffusible part α must be pictured as dissolved in the less diffusible part β.

II. Rubber, a Liquid Solvent

The intersolubility or the miscibility of α and β rubbers in each other makes it necessary to regard the product formed by their ensemble as a solvent not only of the more diffusible hydrocarbon of rubber but also of many other hydrocarbons or compounds having a marked affinity for rubber. Rubber, as well as other similar colloidal substances such as gelatin, cellulose esters, etc., must therefore be considered a solvent of numerous substances in which these substances are capable of ultimately dissolving, if their swelling can be carried far enough. We have shown[5] that rubber, vulcanized or not, behaves in osmotic phenomena like a solvent toward hydrocarbons, in the same way that water acts toward ammonia in the theoretical experiment of Nernst on the osmosis of gases. The theory of solid solution applied to the swelling phenomenon has also been recently upheld by Katz.[6] With respect to the solubility of gases and in particular of carbon dioxide, it has been known for a long time, and Wroblesky[7] has shown that the Henry law for the dissolution of gases is applicable to rubber, which dissolves carbon dioxide and nitrogen monoxide in quantities which are linear functions of the temperature. The

conclusion that can be drawn has since been confirmed in various ways, among others by Venable and Fuwa.[8] The solubility of certain solids such as sulfur and resins is similarly shown by the osmotic properties of rubber membranes[9] and by the early experiments of Weber, which have since been confirmed recently by Dannenberg,[10] Hauser and Hünemörder,[11] etc.

The three interesting articles published recently by Stamberger on the swelling of rubber under various experimental conditions have led him to two results among many others about which we wish to make some observations, not on the results themselves, which are of very great importance, but on the conclusions which the author believed he was justified in drawing with respect to the polymerization of rubber.

In comparing the swelling power in benzene and chloroform of (1) raw rubber and (2) the same rubber highly masticated, Stamberger[12] proves that the relative magnitude of swelling in the liquid and in its vapor is very different in the case of sample (1) and sample (2). The ratio for the swelling of the first sample is about 16, whereas

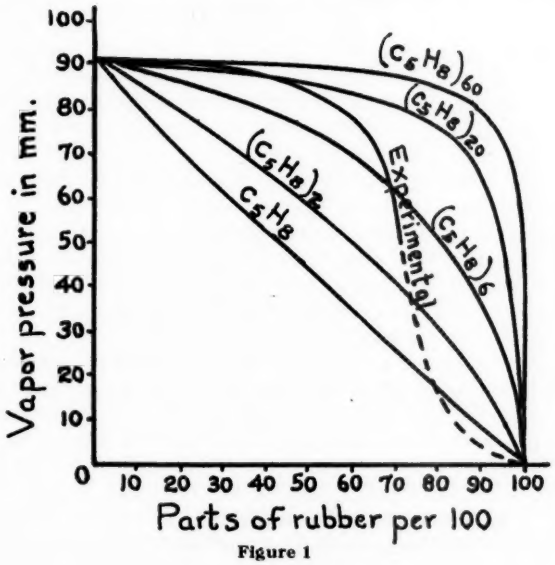

Figure 1

it is less than 2 for the second. The observer does not fail to mention, moreover, that such a fact cannot be explained by the various theories of the constitution of jellies.

The second proof made by Stamberger[13] is that the vapor pressure of rubber jellies does not follow the Raoult law, which requires that the relative diminution of the vapor pressure be proportional to the quantity of dissolved substance it contains. Furthermore, the vapor pressure of these jellies is, at each concentration, independent of the degree of mastication undergone by the rubber used.

The Raoult law was first established experimentally for the true solution of a solid in a liquid. It was then obtained theoretically on the basis of thermodynamics by the hypothesis where the two substances which constitute the solution have a constant molecular weight and are finely mixed without change in volume, forming a single liquid.

The relation is then found to be:

$$\frac{p_0 - p_1}{p_0} = c\,\frac{n_1}{n_0 + n_1},$$

p_0 and n_0 being the vapor pressure and the number of molecules of solvent, respectively, p_1 and n_1 the same values for the dissolved substances; c is a constant of approximately 1, which can be disregarded in this discussion.

According to this formula, p_0 and p_1 being determined experimentally, n_1 can be calculated if n_0 is known; or inversely, an examination of the results shows immediately that the method is inapplicable to the measurement of molecular weights in jellies, either for the dissolved liquid or for the dissolving colloid. The Raoult law in this case is wholly inapplicable, but in fact this case is far removed from the liquid crystalloidal solutions for which it is applicable.

Figure 1 shows the experimental values found by Stamberger for the vapor pressure of rubber-benzene jellies. In finer curves we have shown on the same diagram the values calculated by the formula

$$p_1 = p_0\,\frac{n_0}{n_0 + n_1}$$

which result from the formula given above, giving different hypotheses on the size of the rubber molecule. The curves show the difference between the general course of the experimental curve and the curves resulting from calculation on the supposition of a constant degree of polymerization of the rubber for molecular weights of 68, 136, 408, 1360, and 4080, successively.

Such a lack of agreement between the results with jellies and those with true solutions of crystalloidal substances proves that we are wholly ignorant of the manner in which the dissolution of colloids takes place and, in any case, that the comparison of these solutions with others is an error to be guarded against. The two types of solutions differ in an important factor, rigidity. A true liquid cannot, by definition, possess any rigidity. One is not warranted in applying to jellies, whose rigidity is often considerable, theories relating to liquid mixtures.

The conclusions which can be drawn from experiments on vapor pressure of jellies are then vitiated by errors due to the single fact that the interpretation given to the experimental results depends on a theory that is obviously not applicable in this case. However, the very interesting observation according to which there is no difference between the vapor pressures of two rubber jellies, one made from raw rubber and the other from the same rubber which has been highly masticated, has led the author to question the theory of polymerization.

In the swelling of raw rubbers by a solvent and their diffusion in the solvent, one easily understands that the "framework" of the rubber, or its non-diffusible part, represents only a very small part of the weight of the entire substance; it follows that even while admitting that the number of rubber molecules may have an overwhelming influence on the vapor pressure of the jelly, this number is only very slightly modified by the breaking of the "framework" into smaller molecules. Because of this, the differences observed in measuring vapor pressure may be less than the experimental errors.

It does not appear admissible, in any case, to conclude from this experiment in favor of the opinion of Harries, who assumes the existence in the case of rubber of a definite hydrocarbon, since the curve in Fig. 1 shows results entirely different from the values calculated with this hypothesis.

III. The Absorption of Liquids and Vapors by Rubber

The errors, which one may commit by insufficiently justified comparisons of the adaptation of one phenomenon to another are especially noticeable in the rela-

tive swelling of a single colloid such as rubber in a liquid solvent or in the saturated vapor of this solvent at the same temperature. For example, if we take two samples of vulcanized rubber and place one in benzene at room temperature and the other in a closed tube containing benzene whose vapor alone is in contact with the rubber, the well-known fact is observed that swelling in the liquid is much greater and much more rapid than in the vapor. Besides, the rubber which has been swollen in the liquid and left in contact with the saturated vapor losses it swelling progressively until it reaches the limiting volume which it is capable of attaining in the vapor.

Von Schröder,[14] who was the first to point out this phenomenon in the case of gelatin, considers it apparently incompatible with the second law of thermodynamics. If, in fact, a piece of gelatin is immersed in water, or a piece of rubber in benzene, in such a way that part of the jelly sticks out of the liquid, the portion in contact with the vapor loses little by little its absorbed liquid of swelling, which will be taken up again by the portion submerged in the liquid. There would thus be a perpetual motion. This latter fact does not correspond to anything actually taking place.

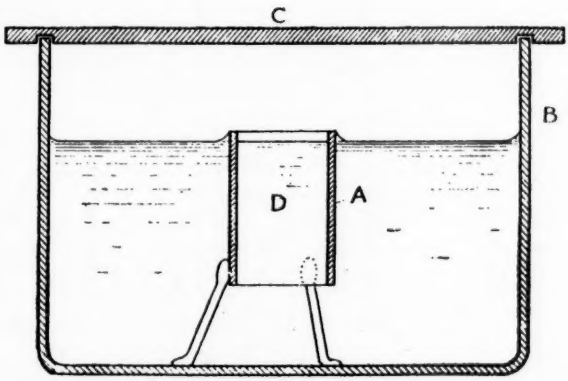

Figure 2

In fact, we have carried out the following experiment. A small glass tube, *A* (Fig. 2), open at both ends, is mounted on three legs which allow it to rest in a vertical position; this tube is placed in a glass dish, *B*, which can be hermetically sealed by a cover *C*. The tube *A* is filled with a jelly, of gelatin for example, containing about 25% gelatin, water is run into box *B* until it has the same level as the top layer of gelatin *D*.

This is then let stand for several weeks, protected against too great heat. Observations taken from time to time prove that there is never a swelling of the jelly in the upper part, but only in the part submerged in the liquid. At the end of the experiment, the appearance of the jelly in the small tube has changed from the form *a* of the beginning to the form *b*. (See Fig. 3.) As can be seen, the upper level is simply raised up a little by the pressure, due to the swelling of the gelatin lying below it, but at no time during the entire experiment did the upper layer absorb enough water to be in such a condition that it was susceptible of losing it by evaporation into the saturated vapor. There was in fact a considerable difference between the rigidity of the jelly in the upper and lower parts of the small tube. In the small tube the swelling increases progressively from the bottom to the top in such a way as to reach a state of equilibrium which varies from one level to another. There

is a swelling of the jelly in the liquid, but once equilibrium is reached, evaporation from the liquid into the vapor never takes place, because the concentration of the jelly remains below the proportions required for the evaporation to take place. There is, therefore, no reason to assume that in the permanent state there is a continuous circulation of the liquid, as the experiment shows.

The important point in this problem is that the maximum swelling in the liquid is not the same as in the vapor, and this fact is easily understood. The surface tension of the jelly in contact with water is very different from that in vapor, and it is only natural that the swelling itself should be different.

The only fact of which the explanation remains uncertain is that of the evaporation of the excess liquid of swelling in saturated vapor. In order for this evaporation to take place the vapor pressure of the jelly must be greater than the pressure of the pure liquid. Everything occurs in fact as if the vapor pressure of the jelly varies with the proportion of liquid in such a way that it becomes equal to that of the saturated vapor for the proportion corresponding to the equilibrium in the vapor itself, lower for weak proportions and higher for high proportions. The experiments carried out by us to demonstrate that this vapor pressure of jellies is greater than that of the liquid have completely failed, and we understand the reason for this failure, knowing the causes of the excess of vapor pressures of jellies.

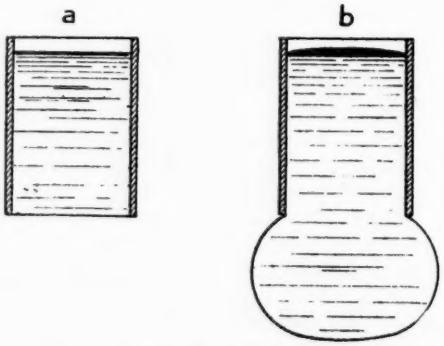

Figure 3

Wiedmann and Lüdeking[15] have pointed out that the swelling of colloids causes an evolution of heat at the beginning, but if the swelling is stopped at a certain point and the jelly obtained is submitted to swelling in its turn, this second action takes place with cooling. For example, if five times its weight of water is added to a dry gelatin the reaction is exothermic (+3 calories). On the contrary, if to a two per cent jelly of gelatin four times its volume of water is added, the phenomenon is endothermic (−10 calories). The same facts are observed with gum arabic, dextrin, gum tragacanth, starch, and tannin. It is a general phenomenon which suffices to explain the apparent paradox of reduction of swelling in vapor.

When a colloid which has been greatly swollen in liquid is put into vapor, its weight changes but slowly. The phenomenon which takes precedence of all others is syneresis, by which the jelly tends slowly and progressively to contract while exuding a part of the liquid it contains. The decrease in swelling is in this case accompanied by heat evolution, the temperature of the jelly becoming slightly higher than that of its medium; the vapor pressure of the liquid expelled is greater than that of the liquid in the lower part of the vessel and distillation occurs.

It is easily seen that the direct measurements we have attempted to make of the vapor pressure of the jelly in comparison with that of the swelling liquid (measurements in which constant temperatures must be maintained in the jelly and in the liquid) prove nothing, since the difference in pressure must depend upon a difference in temperature. Moreover this difference may be very slight, because the time required for reduction of swelling by evaporation is very great.

In regard to the difference in swelling in the liquid and in its saturated vapor, it is interesting to note that the only difficulty encountered in explaining this phenomenon in a simple way arose from the point of departure generally adopted, either in considering the jelly as a gel, that is, a two-phase system where the liquid is retained in the capillary spaces only by the effect of surface tension, or in assuming the existence of a true solution. The important factor of solvation is omitted.

IV. Variations in Heat Accompanying Swelling

We have just called attention to the fact that swelling is accompanied in the beginning by evolution of heat and later by absorption of heat. This fact leads to the prediction that the dissolution of the swelling liquid in rubber is made up of two superposed reactions, of which the first part prevails over the other during the first part of the process, and later the second becomes predominant when swelling is greater.

In a series of papers published in 1928,[16] we have shown in some detail that the large majority of properties of colloidal substances can be explained by the hypothesis of a variation in the degree of polymerization of the substances, accompanied by solvation. It has in fact been verified, so far as swelling is concerned, that this phenomenon does not follow the usual laws of the solution of crystalloids, even taking into account the changes brought about by the diffusion of the liquid in the colloidal mass, a diffusion which does not occur in ordinary solutions[17] which can be agitated. Although the physical changes produced by swelling are very important, they are not sufficient to explain the special character of the law governing the speed with which the swelling is produced. No reasons can be seen which justify the difference between theory and experiment, except that of the existence of chemical reactions accompanying swelling. It seems natural, therefore, to assume that during the increase in volume, at least when it exceeds a certain amount, there is a rupture of the molecular chains of the colloid and a fixation of the chemical radicals present in the dissolving liquid by the affinities thus made available.

Swelling, regarded from this point of view, becomes a complex phenomenon resulting from the dissolution properly called, from a chemical reaction of polymerization, and from simultaneous solvation. Thus one understands the fact, frequent enough but none the less surprising, that such a substance which is capable of swelling feebly in two liquids taken separately, swells greatly and even disperses in a mixture of these two liquids.

In order to obtain dissolution, the liquid used as a solvent must have the double property of not only an infinity for the solid substance which brings about dissolution, but also a power of chemical reaction, producing solvation.[18] A solvent must be composed of two liquids when one of these liquids does not possess the power to diffuse into the colloid and the other does not have the power to split the bonds which limit swelling, its own diffusion into the colloidal substance being brought about by means of the first solvent but either not at all or only in a very feeble manner in the absence of the latter.

Numerous examples are found to justify the double action of solvents, but as they do not concern rubber it will be sufficient here to mention only that of nitrocellulose. Water acts toward this substance as it does toward cellulose itself, *i. e.*,

as an agent of solvation but not as a solvent. It is present, in more or less large proportions, in ordinary pyroxalins. By solution in acetone which dissolves the water, the water is replaced by the new solvent whose power of solvation is greater than that of water. If the solvent is then evaporated, the water is entrained over in the evaporated substance, and in the absence of the agent of solvation nitrocellulose is obtained with a degree of polymerization much higher than that of the original product. MacBain, Harvey, and Smith[19] have in fact stated that the solution of this nitrocellulose is much more difficult than that of the first.

Considering the phenomenon of swelling as a double action of (1) the diffusion of liquid in rubber and (2) the solvation carried out by this liquid, then one includes this substance in the same group of properties which one ascribes to lyophilic colloids in general, and some of the difficulties encountered with the various hypotheses on the constitution of rubber are explained in a simple way. Thus is explained, particularly in the case with which we are concerned, the fact of an exothermic action at first, followed by one that is endothermic.

V. Continuous Increase of Swelling in Liquids

In a recent work published by J. R. Scott[20] on the swelling of vulcanized rubber in liquids, the author called attention to a fact already observed but which does not seem to have received the importance that it deserves. The curve of swelling as a function of the time, instead of continuing to a maximum value where it remains constant, continues its rise very slowly but in an uninterrupted manner as a linear function of the time. A more complete study of this phenomenon has shown that this increase beyond the false maximum, attained more rapidly and considered up to now as saturation, is independent of the first part of the curve, both from the point of view of the magnitude of swelling and from the time required for it to take place. It depends on the nature of the rubber-liquid system. Scott concludes that these results must be interpreted by regarding the swelling as formed by two superposed and simultaneous processes:

(1) Saturation of rubber by the liquid until it reaches a maximum swelling, and

(2) A slow increase which must be considered as a progressive change in the properties of the rubber.

With vulcanized rubbers of different compositions, the greatest increase is produced in mixtures containing substances favorable to depolymerization, or oxidizing agents, antioxygens having on the contrary the opposite effect. The increase in swelling is then related to a depolymerization produced by the swelling and aided by the oxidizing agents. This effect should commence with the beginning of swelling and should superpose itself on the purely physical phenomenon.

The influence of the liquid which causes swelling is made evident in the magnitude of the maximum of this swelling, which diminishes with the amount of combined sulfur. But this diminution, as Boiry has observed,[21] is very large for saturated hydrocarbons, smaller for aromatic hydrocarbons and still less for liquids containing polar groups. This characteristic also confirms the opinion that the end of swelling is aided by solvation.

It is therefore of interest to note in connection with the subject in which we are concerned that depolymerization produced in swelling, even by a cause secondary to the swelling itself, is manifest in an increase in the volume of the liquid absorbed. In this case, as in that studied in paragraph IV above, neither the theories which consider colloidal substances as porous substances capable of imbibing the liquid by capillarity nor those which depend on the existence in the rubber of two substances of different but invariable polymerization dispersed in one another can explain the facts acceptably.

VI. Contraction of Rubber by Swelling

We are now carrying out a series of experiments to determine the contraction produced during the swelling of rubber and of other colloidal substances by inversion in liquids.

The method used consists in suspending a sample of the substance to be studied in a small vessel suspended in turn on the beam of a balance with a dampener, A, and the readings of which can be made microscopically to the 0.10 mg. on a scale, B. Figure 4 shows schematically the arrangement used, which is not unlike that used in the measurement of densities by the hydrostatic balance. The rubber, cut into small pieces, is put in the cup of glass, C, after all substances soluble in the liquid selected to produce the swelling have been extracted, and the cup is immersed in the liquid, which may be benzene or toluene or any other substance of a lower density than that of the rubber sample.

The weight of equipment C in the liquid is determined previously and the weight the rubber should have if its swelling is produced without variation in volume. The weight is then equalized by an equivalent load, D, on the other arm of the beam. The cup is plunged into the liquid with the necessary precautions so that no gas adheres to the rubber. All that is then necessary is to take readings as a function of the lapsed time from the moment of immersion.

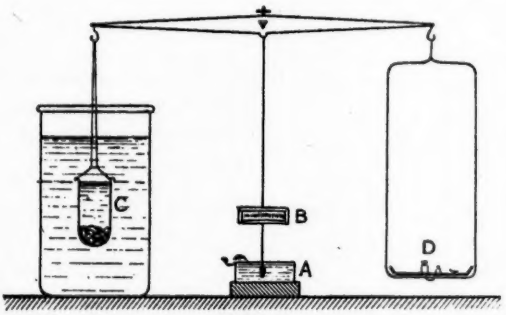

Figure 4

It is clear that if there is no variation of volume during swelling, there will be no variation in weight. The displacements read on the scale permit, therefore, the variation in volume to be calculated directly.

If p is the weight measured, P and V the weight and the volume of rubber, P_1 the weight of the equipment in the liquid and d the density of the liquid, then

$$p = P_1 + P - Vd$$

whence

$$V = \frac{P_1 + P - p}{d}$$

An increase in the resulting weight p therefore corresponds to a reduction in volume.

By way of example, we give the results obtained in applying this method to the swelling in toluene of a vulcanized rubber (red inner tube). The curve of Fig. 5 gives the contraction in thousandths of the volume of rubber. It shows how rapid the contraction during the first minutes is, and that it then reaches a constant value after two or three hours of immersion. Although the swelling of the rubber is still far from complete, the volume of rubber no longer changes, as has been confirmed

after 1240 and 1440 min. The weight of the toluene absorbed was then 3.424 times that of the rubber.

Other determinations have been made on pale crepe dissolved in carbon tetrachloride. The rubber and carbon tetrachloride were both placed in the glass cup suspended on the balance and the whole system was immersed in water. The contraction observed was similar to that in the preceding experiment, *i. e.*, very rapid at first and then coming rather quickly to a constant value. In this case we have not observed any diminution of the contraction with strong swelling, not even for the dissolution of the rubber.

The important point in these measurements is to maintain as constant a temperature as possible, because the corrections to be made if the temperature varies soon become as large as the recorded variations.

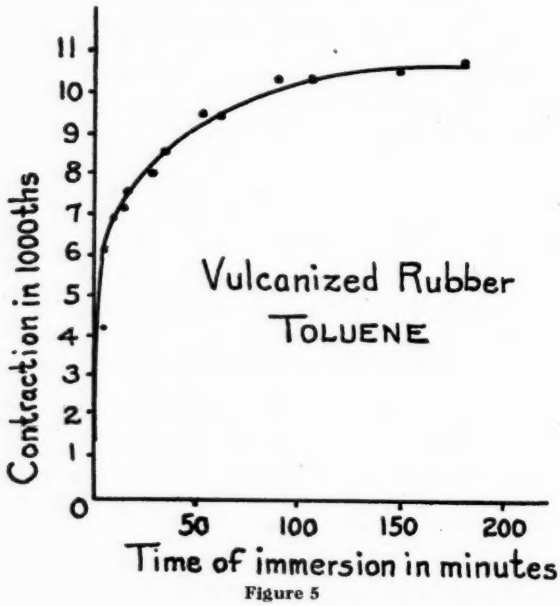

Figure 5

Our object in carrying out these measurements was to verify that the phenomenon of contraction corresponding to the exothermic period of swelling did not have an effect corresponding to the endothermic period which would have been able to show itself by expansion. Moreover, this effect, which has never been described, was not observed.

One is therefore able to conclude that if heating during the first part of swelling has a physical cause, concomitant with contraction, cooling which is brought about by a high degree of swelling or by solution has another cause, and this fact is not in disagreement with what solvation would be able to produce.

VII. Conclusions

In various publications we have previously shown that in many cases it is advantageous to consider jellies as formed of a polymerized colloidal substance, the length of the molecular chains being easily changed according to the conditions

of the system and unlike one another at all times in a single sample. These chains retain free affinities at their extremities to which can be linked so-called solvating groups arising from the solvent or from soluble substances contained in the jelly.

The present work refutes the interpretation given to recent experiments on the vapor pressure of jellies and confirms in certain new ways this constitution.

(1) The experiments of Stamberger on the vapor pressure of rubber jellies and their consistency before and after a prolonged mastication do not support the Harries hypothesis on the stability of the rubber molecule, but merely show that the theory of true liquid solutions is not applicable to jellies.

(2) Based on the idea that polymerization changes with solvation, it is easily shown that the relative swelling in a solvent and in its saturated vapor are not contradictory with the principles of thermodynamics, as it would seem, but on the contrary proceed normally and could have been predicted.

(3) In the study by Scott on the slow but unlimited swelling of rubber beyond the saturation point, this author has come to assume that swelling is a double phenomenon, which confirms our point of view.

(4) The experimental study of the contraction of rubber during swelling shows that this effect does not change its sign at any moment and that consequently the change of sign of the heat evolved in this same process has a cause distinct from that of the initial swelling; perhaps it is to be attributed to the chemical phenomenon of solvation.

References

[1] Feuchter, *Kolloidchem. Beihefte*, **20**, 9, 434 (1925).

[2] Bary and Fleurent, *Compt. rend.*, **184**, 947 (1927); *Rev. gén. caoutchouc*, **4**, No. 31, 3 (1927).

[3] Hauser and Rosbaud, *Kautschuk*, **3**, 17 (1927); Hauser and Mark, *Kolloidchem. Beihefte*, **22**, 63; **23**, 64 (1926).

[4] Bary and Hauser, *Kautschuk*, **4**, 96 (1928); *Rev. gén. caoutchouc*, **5**, No. 42, 3 (1928).

[5] Bary, *Compt. rend.*, **152**, 1386, 1766 (1911).

[6] Katz, *Gesetze der Quellung*, **1916.**

[7] Wroblesky, *Wied. Ann.*, **43**, 544 (1891).

[8] Venable and Fuwa, *Ind. Eng. Chem.*, **14**, 139 (1922).

[9] Bary, *Compt. rend.*, **152**, 1766 (1911); *8th Congres Chimie Appliquée*, **9**, 7 (1912) (New York).

[10] Dannenberg, *Gummi-Ztg.*, **1927**, 1806.

[11] Hauser and Hünemörder, *Caoutchouc & gutta-percha*, **25**, 14146 (1928).

[12] Stamberger, *Rec. trav. chim.*, **47**, 316 (1928).

[13] Stamberger, *J. Chem. Soc.*, **302**, 2318 (1929); Stamberger and Blow, *Nature*, **124**, 13 (1929).

[14] Schröder, *Z. Phys. Chem.*, **45**, 75 (1903).

[15] Wiedmann and Lüdeking, *Ann. Phys. Chem.* [2] **25**, 145 (1885).

[16] Bary, *Chimie des Colloïdes*, Paris, **1929.**

[17] Bary, *Rev. gén. colloïdes*, **4**, No. 37, 322 (1926); *Rev. gén. caoutchouc*, **3**, No. 26, 5 (1926).

[18] Bary, *Caoutchouc & gutta-percha*, **25**, 14464 (1929).

[19] MacBain, Harvey, and Smith, *J. Phys. Chem.*, **30**, 312 (1926).

[20] Scott, *Trans. Inst. Rubber Industry*, **1929**, 95.

[21] Boiry, *Caoutchouc & gutta-percha*, **20**, 12010 (1923).

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Isoprene and Rubber

Part 20.[1] The Colloidal Nature of Rubber, Gutta-Percha, and Balata

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I. The Molecular Weight of Rubber, Gutta-Percha, and Balata

In the preceding work[1] the molecular weight of rubber and balata was calculated on the basis of relations between specific viscosity η_{sp} and molecular weight which are shown by semi-colloidal decomposition products, on the assumption that this relation is also true for eucolloids. The value η_{r-1} was taken as the specific viscosity, *i. e.*, the characteristic viscosity increase[2] of a substance of definite concentration and known solvent.

The expression "specific viscosity" has already been used by J. Duclaux.[3] In viscosity investigations of nitrocellulose solutions he represents this by a constant K which is calculated from the relations of the change of viscosity at various concentrations derived by Arrhenius:[4]

$$\eta_r = 10^{kc} \quad \text{or} \quad K = \frac{\log \eta_r}{c} \tag{1}$$

Based on these constants, nitrocelluloses show different average molecular weights for the increase in viscosity, that is, this constant K is greater with high molecular products than with low. In the following, this constant represents not the specific viscosity, but the viscosity-concentration constant K_c; the earlier constant K_m which, on the basis of the formula:

$$\eta_{sp} = K_m c M \tag{2}$$

expressed the relation between the specific viscosity and the molecular weight, is called the viscosity-molecular weight constant.

No relations between the viscosity-concentration constant and the molecular weight can be found in the Duclaux experiments, since the molecular weight of nitrocelluloses was not known in any instance. Moreover with semi-colloidal polysterols, the higher the molecular weight the more rapidly does the viscosity increase with increasing concentration. This is shown in curves[5] which have already been published. As will be reported elsewhere,[6] a constant is obtained for various polysterols on the basis of the Arrhenius-Duclaux formula, which stands in simple relation to the molecular weight. From this the unknown molecular weight of the eucolloidal polysterol can be calculated by the following formula:

$$M = K_c \times 10^4 \tag{3}$$

This viscosity-concentration constant K_c was now calculated[7] for several semi-colloidal decomposition products of rubber and gutta-percha (see Tables I, II, III, and IV).

TABLE I

SEMI-COLLOIDAL DECOMPOSITION PRODUCTS OF GUTTA-PERCHA

Average Molecular Weight, 2400

c	η_r	η_{sp}/c	% Deviation from η_{sp}/c	K_c
0.25	1.2	0.8	..	0.31
0.5	1.48 [8]	0.96	20 [8]	0.34 [8]
1.0	2.31 [8]	1.32	65 [8]	0.36 [8]

TABLE II

SEMI-COLLOIDAL DECOMPOSITION PRODUCT OF RUBBER

Average Molecular Weight, 3300

c	η_r	η_{sp}/c	% Deviation from η_{sp}/c	K_c
0.25	1.26	1.04	..	0.40
0.5	1.55	1.10	6	0.38
1.0	2.29	1.29	24	0.36

TABLE III

SEMI-COLLOIDAL DECOMPOSITION PRODUCT OF RUBBER

Average Molecular Weight, 4200

c	η_r	η_{sp}/c	% Deviation from η_{sp}/c	K_c
0.25	1.29	1.16	..	0.44
0.5	1.66	1.32	14	0.44
1.0	2.83	1.83	58	0.45

TABLE IV

SEMI-COLLOIDAL PRODUCT OF GUTTA-PERCHA

Average Molecular Weight, 6500

c	η_r	η_{sp}/c	% Deviation from η_{sp}/c	K_c
0.25	1.50	2.00	..	0.70
0.5	2.15	2.30	15	0.66
1.0	4.30	3.30	65	0.63

These tables show that here also, as with polysterols, there is a relation between the viscosity-concentration constant K_c and the molecular weight, and, in fact, they both change in rough proportion to one another. In a first approximation, one can therefore use[9] Formula 3 above, which was obtained with polysterols for the calculation of the unknown molecular weight of eucolloidal rubber and of balata.

If one calculates on the basis of measurements given in the previous work the viscosity-concentration constant K_c for rubber fractions purified according to Pummerer's method and for purified balata, the following values are obtained:

TABLE V

RUBBER, PURIFIED ACCORDING TO PUMMERER'S METHOD

Easily Soluble Fraction

c	η_r	η_{sp}/c	% Deviation from $_{sp}/c$	K_c
0.01	1.157	15.7	..	6.3
0.025	1.389	15.5	..	5.7
0.05	1.911	18.2	16	5.6
0.1	3.436	24.2	54	5.3

TABLE VI

RUBBER, PURIFIED ACCORDING TO PUMMERER'S METHOD

Difficultly Soluble Fraction

c	η_r	η_{sp}/c	% Deviation from η_{sp}/c	K_c
0.01	1.220	22.6	..	8.6
0.025	1.543	21.8	..	7.5
0.05	2.442	28.9	31	7.7
0.1	4.565	35.7	63	6.6

TABLE VII

BALATA FROM LATEX

c	η_r	η_{sp}/c	% Deviation from η_{sp}/c	K_c
0.01	1.159	15.9	..	6.4
0.025	1.386	15.4	..	5.7
0.05	0.773	15.5	..	5.0
0.1	2.870	18.7	17	4.6
0.25	8.575	30.3	90	3.7

From these are obtained the following molecular weights:

TABLE VIII

	$M = K_c \times 10^4$	$M = \eta_{sp}/cK_m$
Rubber, easily soluble fraction	56,000	52,000
Rubber, difficultly soluble fraction	77,000	73,000
Balata from latex	51,000	52,000

In addition, a raw rubber (Table 9) and a masticated rubber (Table 10) were studied.[10]

TABLE IX

CREPE RUBBER

Molarity	Rate of Flow in Sec. (Benzene = 33.5)	η_r	η_{sp}/c	% Deviation from η_{sp}/c	$K_c = \log \eta_r/c$
0.0125	56.5	1.68	54.4	..	18.0
0.025	89	2.65	66.0	21	16.9
0.05	215	6.41	108.2	100	16.2
0.1	820	24.4	234.0	330	13.9
0.2	8537	254.8	1268.0	2200	12.0[10a]

TABLE X

MASTICATED RUBBER

Molarity	Rate of Flow in Sec. (Benzene = 33.5)	η_r	η_{sp}/c	% Deviation from η_{sp}/c	$K_c = \log \eta_r/c$
0.025	40.0	1.19	7.6	..	3.0
0.05	47.9	1.43	8.6	13	3.1
0.1	67.6	2.01	10.1	33	3.0
0.125	101.3	3.1	16.0	110	3.8
0.25	241.3	7.2	24.8	226	3.4
0.5	860.5	25.6	49.2	650	2.8
1.0	7135.0	213.0	212.0	2700	2.3[10a]

From these values the molecular weight can be calculated in two ways: first, from the viscosity-concentration constant K_c, second, from the viscosity-molecular weight constant K_m. In the latter case, values obtained in very dilute solutions must be used for the calculation, and the viscosity measurements are carried out at concentrations where the molecules are still in free motion (see Part 4).

For the two products itemized below, the following general orders of magnitude were obtained for their molecular weights.

TABLE XI

	$M = K_c \times 10^4$	$M = \eta_{sp}/cK_m$ ($K_m = 3.0 \times 10^{-4}$)
Hevea rubber.....about	160,000	180,000
Masticated rubber	30,000	25,000

Tables VIII and XI show that the molecular weights obtained by both methods agree in their order of magnitude. They correspond as well to the values which Wo. Ostwald[11] calculated from osmotic measurements carried out by Caspari.[12]

TABLE XII

	Molecular Weight = Limiting Value of Micelle Weight, According to Ostwald
Rubber, fresh	129,000
Rubber, partly depolymerized	84,000
Gutta-percha	37,000

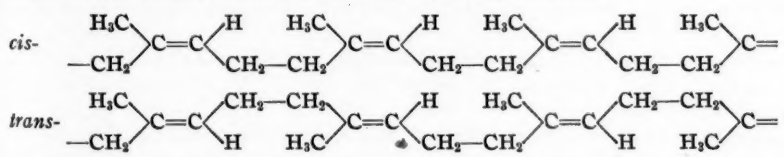
Based on the viscosimetric measurements the average molecular weight of the balata[13] obtained from latex is higher than that of gutta-percha according to the measurements of Caspari. This may depend upon the fact that the gutta-percha of Caspari had already been somewhat decomposed by oxidation. Furthermore, the raw rubber shows a higher average molecular weight than that purified by Pummerer's method; during the purification a partial decomposition of the rubber molecule occurs, as will be shown by a later work.[14] The particularly high viscosity of raw rubber solutions is therefore due not wholly to its content of proteins and other impurities, as has been assumed many times.

It is of interest that masticated rubber has an essentially lower molecular weight than crepe rubber. Mastication does not, therefore, consist in a diminution of the size of the micelle, but rather in a diminution of the molecules.[15] This may result from the fact that in the milling process the long chains are ruptured[16] mechanically. It is also possible, however, that decomposition is brought about by atmospheric oxygen, in a similar manner to that of balata[17] described in the previous work. Which of these two phenomena plays the essential role can be ascertained only by studies of the mastication of pure rubber carried out with complete exclusion of air.[18]

II. The Constitution of Rubber, Gutta-Percha, and Balata

According to the foregoing molecular weight determinations, the differences between rubber on the one hand and gutta-percha and balata, which are essentially identical,[19] on the other hand, do not depend solely on a different size of the molecules, for a somewhat decomposed rubber having the same average molecular weight as gutta-percha and balata still possesses about the same properties as the original rubber, and in contrast to gutta-percha and balata shows, for example, no tendency to crystallize. Furthermore, these differences between rubber, gutta-percha, and balata remain in their semi-colloidal decomposition products. It has already been pointed out[20] that there are two series of homologous polymeric polyprenes, rubber, and its semi-colloidal decomposition products on the one hand and gutta-percha and balata and their decomposition products on the other hand.

According to the experiments carried out up to now the difference between these two series depends upon the fact that gutta-percha and balata are the *cis*-modifications of polyprenes, while rubber is the *trans*-modification.[21]



One is led to this concept by the observation that, after reduction of the double bonds, the differences between the two series disappear: hydro-rubber, hydro-gutta-percha, and hydro-balata have the same appearance.[22]

Rubber is given the *trans*-form, balata and gutta-percha the *cis*-form, for the following reasons: the specific gravity of crystallized balata[23] is greater (d_{20} =

0.9571)[24] than that of amorphous rubber[25] (d_{20} = 0.9238).[24] The symmetrical molecules, that is, those of the *cis*-form, are packed more densely in a solid state than those constructed unsymmetrically. Above all the crystallization of balata and gutta-percha points to their molecules having a more symmetrical structure than that of rubber, since the latter does not crystallize out of solution. Based on many experiments, the ability of high molecular products to crystallize depends upon their symmetrical structure and not upon the length[26] of their molecules. Crystallization is therefore to be considered as a parallel arrangement of long thread-like molecules and a symmetrical structure of the chain with a lattice arrangement of the atoms.

III. The Form of the Rubber, Gutta-Percha, and Balata Molecule

In a whole series of examples, it has been shown up to now that with semi-colloidal products the specific viscosity rises proportionately to the molecular weight.[27] This relation is comprehensible only on the assumption that the thread-like molecules present in solution correspond to rigid threads and do not represent spirally rolled or coiled forms.

This remarkable conclusion about the form of the molecule is proved in still another way: first through the ability of high molecular substances to crystallize from solution, and, second, the ease of crystallization of balata from solution would not be comprehensible if its thread-like molecules were not rigid. Also in further agreement with this is the fact that liquids also show x-ray interferences which change in homologous series in proportion to the molecular length.[28] If the form of the molecules of liquid substances were not rigid but variable, then these relations would not be true.

Finally the important observation that the fragility of the molecule increases with increase in its length is in agreement with the concept of rigid molecules. Thus the long rubber molecules are more sensitive and are more easily ruptured with increase in temperature than the shorter molecules of gutta-percha and balata. The molecules of all these products are still more unstable than the relatively short molecules of a semi-colloidal polyprene.[29] If the molecules in solution correspond to flexible fibers, then no differences should occur in the stability with increasing length, exactly as the strength of cotton fibers remains the same for different lengths. On the other hand, the fragility of a thin, rigid glass fiber increases greatly with increasing length when shocked; therefore it is also easy to understand why a single rigid molecule on account of the vibrations of the atoms is much more brittle than a short one.[30]

The rubber molecule cannot in principle be constructed in any different way from the molecule of gutta-percha and balata, although the rubber does not crystallize, for if it were, the viscosity-molecular weight constants of the semi-colloidal decomposition products of both series would not be in approximate agreement. One must therefore assume that the rubber molecule is an approximately rigid fiber and also that in the solid state these rigid fibers have a parallel alignment.[31] As a result of the asymmetric structure of the molecule, crystallization cannot take place directly, however.

Various investigators have assumed that in a rubber molecule the atoms are arranged spirally. Only by stretching of the spirals should it be possible to bring about a lattice arrangement of the atoms. This peculiar form of the molecule, in connection with the double bonds contained in the molecule, should explain its elasticity.[32] Such simple relations between the structure of the rubber molecule and its elastic properties may not exist. It has already been suggested[33] that the eucolloid polysterol, which lacks elastic properties when cold, is elastic at 100°,

although it does not have double bonds. Recently Kern has observed in this laboratory that certain modifications of the polyoxymethylene have slightly elastic properties at elevated temperatures. Accordingly the elasticity bears no relation to the double bonds in the rubber molecule, but instead it occurs in many high polymeric substances, but of course only within definite temperature ranges. The experiments up to now on synthetic substances show further that a relation exists between the elasticity and the molecular size; in the homologous polymeric series of polysterols the elastic properties increase with increasing molecular size.[34]

IV. The Nature of the Colloidal Solution of Rubber, Gutta-Percha, and Balata

According to our concept[7] there is a gradual transition between low molecular semi-colloidal and macro-molecular (eucolloidal) polyprenes, for all have the same principle of construction in the sense of the Kekulé structure. Opposed to this concept is the fact that between the high molecular substances, rubber and balata, and the low molecular decomposition products, there exist fundamental differences which cannot be ascribed solely to the differences in size of the molecule. Rubber swells, while low molecular polyprenes are dissolved in a normal manner; with colloidal soluble rubber, the osmotic pressure increases with increasing concentration,[35] so that in concentrated solution the molecular weight is apparently smaller than in dilute solutions. Low molecular polyprenes probably behave in exactly the opposite manner: there at high concentrations, the molecular weight may be found to be higher, since association takes place between the molecules. Finally, one is surprised by the extraordinary increase in viscosity shown by eucolloidal solutions when their concentration increases. Thus 0.5-molar solutions, *e. g.*, a 3.4% rubber solution, resemble a jelly rather than a solution. Solutions of similar concentration of semi-colloidal decomposition products of rubber are of lower viscosity and in appearance and behavior resemble a solution of low molecular compounds more than eucolloidal solutions.

This important difference is explained when one imagines that the field of action of the macro-molecule in solution is much greater than that of smaller molecules. In Part 33[36] it was shown that the specific viscosity of solutions of similar concentration of homologous polymeric products is not the same, as one might have expected from the Einstein formula, therefore the relation:

$$\eta_{sp} = K_c \qquad (4)$$

is not valid, for η_{sp} increases rather in proportion to the molecular weight, and therefore Formula 2 is the correct one.

This relation is comprehensible on the assumption that the field of action of the molecules is not proportional to their volume, but increases in proportion to the square of the length of the molecule. If solutions of equal concentration are prepared with various members of the same series of homologous polymers, then the number of molecules decreases with their increasing length in the solution. The field of action of the individual molecules increases, however, with the square of the length. Thus it happens that the field of action of relatively few macro-molecules in a solution is much greater than the field of action of much more numerous semi-colloidal molecules, although the concentration of the solutions is the same. The following calculation shows this: in a 0.1-molar solution, 6.8 g. of a polyprene are dissolved in 1 l.; therefore, in 1 cc. there are, at a degree of polymerization of 1000, 6.06×10^{16} macro-molecules. In order to calculate the field of action of a macro-molecule the following numbers are used as a basis: one isoprene residue in the polyprene chain has a length of about 4.5 Å. U., and the

chain itself is 2 Å. U. wide. If one further assumes that these molecules are not single fibers, but double fibers[37] then the diameter (d) of such a double molecule may be about 6 Å. U., and the length of the molecule (h) amounts at a polymerization degree of 1000 to 2250 Å. U. If one further assumes that the field of action of a molecule is $(h/2)^2\pi d$[38] one arrives at the values in Table XIII which are calculated for a 0.1-base molar, *e. g.*, a 0.68% polyprene soln.

In the sixth column of Table XIII the total field of action of the molecule is given. It is seen that this increases greatly with increasing average molecular weight. Since 1 cc. contains 10^{24} (Å. U.)^3 the field of action of the macro-molecule in a 0.1-molar rubber solution of a molecular weight of 170,000 is 3.6 times greater than the volume of the liquid; in a 0.1-molar balata solution having an average molecular weight of 48,000, the field of action is the same as the volume of the molecules. With semi-colloids, on the contrary, the field of action is much smaller than the volume of the solution.

On the basis of these values one can calculate for the various polyprenes the limiting concentration at which the field of action of the molecules takes up all the available space. It is reached with raw rubber in a 0.03 molar or 0.2% solution, with balata in a 0.1-molar or 0.68% solution.

TABLE XIII

Product	Rounded Values for the Average Molecular Weight	Rounded Values for the Degree of Polymerization	Number of Molecules in 1 cc. of a 0.1-Molar Solution	Field of Action of a Molecule in (Å. U.)^3	Field of Action of All Molecules in 1 cc. solns. in (Å. U.)^3	Field of Action as % of the Total Volume of the Solution	Transition from True Solution to Gel Solution at Concentrations in Mol. %	
Raw rubber	170,000	2,500	2.4×10^{16}	1.5×10^{8}	3.6×10^{24}	360	0.03	0.2
Rubber purified by Pummerer's method:								
Difficultly soluble	6,800	1,000	6×10^{16}	2.4×10^{7}	1.5×10^{24}	150	0.067	0.46
Easily soluble	54,000	800	7.6×10^{16}	1.5×10^{7}	1.1×10^{24}	110	0.09	0.61
Balata	51,000	750	8.0×10^{16}	1.3×10^{7}	1.0×10^{24}	100	0.10	0.68
Masticated rubber	27,000	400	1.5×10^{17}	3.8×10^{6}	5.7×10^{23}	57	0.18	1.2
Semi-colloidal polyprene:								
1	6,800	100	6×10^{17}	2.4×10^{5}	1.5×10^{23}	15	0.67	4.6
2	3,400	50	1.2×10^{18}	6×10^{4}	7.2×10^{22}	7.2	1.4	9.5
Low molecular polyprenes	680	10	6×10^{18}	2.4×10^{3}	1.5×10^{22}	1.5	6.7	46.0

In comparison even 1-molar or 6.8% true solutions can be prepared from semi-colloidal polyprenes. Columns 8 and 9 of Table XIII show plainly the great difference between solutions of low molecular and high molecular products.

On the basis of these calculations the differences between low molecular and high molecular substances become comprehensible. High molecular substances are dissolved in a normal manner only at extraordinarily low concentrations. Here, as with low molecular substances, are molecules in solution and not micelles. Both with balata[39] and polysterols,[40] this was proved by the fact that the specific viscosity is not changed at different temperatures. Only within this range of concentration is the osmotic law valid, and the viscosity increases proportional to the concentration, as the Einstein law requires. The colloidal solutions of high molecular substances most often used, the 2 to 5% solutions, which surprise us

by their high viscosity and their anomalous behavior, in which therefore the "colloidal" properties stand out especially strongly, are no longer normal solutions, for in them the molecules no longer move freely. Because these gel solutions are connected with true gels by a continuous series of transition members, this peculiar state of solution should be designated as *gel solution*. It is therefore plain from the above calculations that one can no longer prepare molar solutions (6.8%) from a rubber of average molecular weight of 170,000, because at such a concentration the available space is 30 times smaller than is necessary for the preparation of a true solution. Here the movement of the molecules is already greatly interfered with, and this mixture does not give a solution but a gel, a swollen rubber. The completely diluted solution of macro-molecular colloids, which are to be compared with solutions of low molecular substances, may be designated as *sol solutions*. In a sol solution, therefore, the field of action of the dissolved colloidal molecules[41] is smaller than the total volume of the solution, so that actual solution exists.

Solutions of macro-molecular substances are therefore in fact greatly different from solutions of low molecular substances. There is indeed no essential difference, but only a very gradual one. The different behavior of eucolloidal solutions is thereby explained by the fact that these solutions are not as a rule sol solutions, but gel solutions. In them the molecules are hindered in their movement. Such a solution upon flowing can overcome this hindrance by orientation of the long molecules, and therefore such solutions already show strong deviations from the Hagen-Poiseuille Law. The earlier discovery that the greater the molecular size the greater the deviations is thus comprehensible.[42]

The transition from the gel state to the sol state makes itself evident in a sharp rise in the viscosity, since it is precisely at this point that free movement of the molecules stops. Because the rigid, long molecules come in contact in the solution, they form "barriers" which offer resistance to the normal current, and this is evident in the great increase in viscosity. The limiting concentration at which this increase in viscosity takes place varies with the molecular size; with the largest molecules this limiting concentration lies within the range of a quite dilute solution, with semi-colloids in a relatively concentrated solution. In Table XIV are grouped deviations from the Einstein Law which are shown by various polyprenes at different concentrations.

TABLE XIV

Product	Round Values for Degree of Polymerization	Transition from True Solution to Gel Solution at Concentrations in Mol.	% Deviation from η_{sp}/c at Concentrations in Mol. 0.025	0.05	0.1	0.25	0.5	1.0
Raw rubber	2500	0.03	21	100	330	..	..	..
Rubber purified by Pummerer's method:								
Difficultly soluble	1000	0.067	..	31	63	..	..	..
Easily soluble	800	0.09	..	16	54	..	..	..
Balata	750	0.10	..	..	17	90	..	..
Masticated rubber	400	0.18	..	13	33	226	..	..
Semi-colloidal polyprenes:								
1	100	0.67	..	..	..	..	15	65
2	50	1.4	..	..	..	..	6	24

The sharp rise of the curves[43] always occurs when the deviations from the calculated value of η_{sp}/c are very large. Table 14 shows that the deviations always amount to about 50 per cent if the limiting concentration of the solution is reached when the solution passes over from the sol state to the gel state. As

shown by curves published earlier,[43] the increase in viscosity is much greater for high molecular products than for low ones, and this, as was shown in the first chapter, is manifest in the different values of the viscosity-concentration constant. With quite low molecular substances, very high concentrations must be exceeded in order to pass beyond the sol state. In these highly concentrated solutions other phenomena also appear, *e. g.*, associations of molecules (colony formation). This association of macro-molecular substances takes place only at concentrations where a normal solution no longer exists, *i. e.*, in the range of the gel solution. Therefore these phenomena play a less important part in explaining the anomalous properties than does the remarkable fact of the appearance of the gel solution.

Furthermore, on the basis of these calculations one can understand why only high molecular substances are able to swell, and not similarly constituted low molecular ones. The field of action of a molecule in the dissolved state must be much greater than the volume of the molecule itself, in which case a uniform mixture of large molecules and liquid molecules results, without the latter having completely free motion. The swelling of a highly concentrated solution has been described by Katz in his well-known work.[44] With low molecular substances the field of action of a molecule is scarcely greater than its own volume, so that here normal solution results and no swelling.

Lastly, it can be understood why the osmotic determinations of rubber and other high molecular substances may be carried out only in quite weak concentrations, in which the molecules are normally in solution. For concentrated solutions, not only are the osmotic laws valid but also the swelling laws, and in fact with increasing concentration the swelling pressure increases comparatively rapidly. Because of this, Ostwald[45] has shown that the molecular weight can be calculated on the basis of osmotic determinations, if both factors—the osmotic pressure and the swelling pressure[46]—are considered separately. Wo. Ostwald and other authors[47] call this strong requirement of solvents during solution of high molecular substances *solvation*. This is closely connected with the fact that large molecules, on account of their strong intermolecular force, possess a special capacity for solvation. However, as has already been explained in earlier work,[48] these homopolar macromolecular hydrocarbons, like polysterol and balata, possess no special solvated shell, since the specific viscosity is the same at different temperatures. The anomalous behavior of macro-molecular substances in solution is therefore to be attributed not to a special solvation but to the great field of action of their molecules, the gel state of their solutions.

All the preceding data are naturally only estimations which represent the order of magnitude. They have no claim to precision, because even in viscosimetric measurements of eucolloids phenomena occur, like the deviations from the Hagen-Poiseuille law, which must be taken into consideration. Furthermore, the influence of the solvent remains to be studied more exactly. However, since the preceding measurements were made in very dilute solutions, the values are correct in their order of magnitude. The preceding data give a picture of the character of colloidal solutions and the fundamental difference between them and those of low molecular substances. The whole concept is valid only for homopolar colloidal molecules; in the case of heterogeneous polar colloidal molecules, like albumins, just as with coördinated colloidal molecules, like the polysaccharides, the conditions are far more complicated than in the simple case here depicted.

References

[1] For 19th Communication, see *Ber.*, **63**, 734 (1930).
[2] Staudinger and Heuer, *Ibid.*, **63**, 222 (1930).

[3] Duclaux and Wollmann, *Bull. soc. chim.* [4], **27**, 414 (1920); Baker, *J. Chem. Soc.*, **103**, 1653 (1913); Bary, *Compt. rend.*, **170**, 1388 (1920).

[4] Arrhenius, *Biochem. J.*, **11**, 112 (1917).

[5] Staudinger, *Ber.*, **59**, 3031 (1926); van Rossem, *Kolloidchem. Beihefte*, **10**, 96 (1919).

[6] *Kolloid-Z.*, **50**, No. 1 (1930).

[7] The values are taken from the work of Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

[8] Both values probably depend upon a faulty measurement, since with other hemi-colloidal products of this average molecular weight the deviation of η_{sp}/c in 1 molar solution is not so great. Unfortunately the measurement could not be checked because of autoöxidation of the substance.

[9] The viscosity-molecular weight constant in the polyprene series and polysterol series has about the same magnitude.

[10] From measurements of R. Nodzu.

[10a] The constant K_c agrees in the range of sol and gel solutions only so long as there is no association.

[11] Wo. Ostwald, *Kolloid-Z.*, **49**, 60 (1929).

[12] Caspari, *J. Chem. Soc.*, **105**, 2139; the work of Caspari is misquoted in *Ber.*, **63**, 736, Note 8 (1930).

[13] Staudinger and Bondy, *Ber.*, **63**, 724 (1930).

[14] From investigations of H. F. Bondy.

[15] Klein and Stamberger, *Kolloid-Z.*, **35**, 362 (1924); van Rossem, *Kolloidchem. Beihefte*, **10**, 129 (1919).

[16] Staudinger, *Kautschuk*, **5**, 129 (1929).

[17] Staudinger and Leupold, *Ber.*, **63**, 730 (1930).

[18] Stamberger had several years ago the kindness to masticate a series of different kinds of rubber with complete exclusion of air, but no results were obtained with the samples. A definite answer can probably be obtained only if quite pure rubber is masticated in the presence and in the absence of oxygen. Acknowledgment is made at this time to Stamberger for his assistance. Cf. Stamberger and Blow, *Kautschuk*, **1930**, 22.

[19] Balata and gutta-percha belong to the same homologous polymeric series. Whether these products show a difference in molecular weight, can be decided only if various kinds of latex are treated with complete exclusion of air. Cf. Staudinger and Leupold, *Ber.*, **63**, 730 (1930).

[20] Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

[21] Staudinger, *Kautschuk*, **5**, 129 (1929).

[22] Geiger, *Dissertation*, Zürich, **1926**; Staudinger, *Kautschuk*, Aug.–Sept., **1925**.

[23] Kirchhof, *Kautschuk*, **5**, 175 (1929).

[24] These values were obtained by H. F. Bondy.

[25] Kirchhof and Matulke, *Ber.*, **57**, 1266 (1924); Macallum and Whitby, *Chem. Zentr.*, **1925**, I, 1295. Crystallized rubber has a higher specific gravity than that of amorphous rubber.

[26] Staudinger and Signer, *Z. Krystallographie*, **70**, 193 (1929).

[27] Staudinger and Heuer, *Ber.*, **63**, 222 (1930); Staudinger and Nodzu, *Ibid.*, **63**, 721 (1930); Staudinger and Bondy, *Ibid.*, **63**, 734 (1930).

[28] Stewart, *Chem. Zentr.*, **1928**, I, 639, 2693; II, 1740; Katz, *Z. Physik*, **45**, 97 (1927).

[29] Staudinger and Bondy, *Ann.*, **468**, 1 (1929).

[30] In the crystal these macro-molecules are stable. Cf. Staudinger and Signer, *Ann.*, **474**, 145 (1929).

[31] Staudinger, *Ber.*, **62**, 2902 (1929).

[32] Kirchhof, *Kolloid-Z.*, **30**, 176 (1922); *Kautschuk*, **6**, 31 (1930); Fikentscher and Mark, *Kautschuk*, **6**, 1 (1930); Meyer, *Biochem. Z.*, **214**, 253 (1929).

[33] Staudinger, *Kautschuk*, Aug.–Sept., **1925**; *Ber.*, **62**, 242 (1929).

[34] Staudinger and Machemer, *Ber.*, **62**, 2922 (1929).

[35] Caspari, *J. Chem. Soc.*, **105**, 2139 (1914); Ostwald, *Kolloid-Z.*, **49**, 60 (1929).

[36] *Ber.*, **63**, 222 (1930).

[37] *Helvetica chim. acta*, **12**, 934 (1929).

[38] *Ber.*, **63**, 222 (1930).

[39] Staudinger and Leupold, *Ber.*, **63**, 730 (1930).

[40] Staudinger and Heuer, *Ibid.*, **63**, 222 (1930).

[41] Staudinger, *Ibid.*, **62**, 2893 (1929); Lumi re, *Chem. Zentr.*, **1929**, I, 2023.

[42] Staudinger and Machemer, *Ber.*, **62**, 2922 (1929).

[43] Staudinger, *Ibid.*, **59**, 3031 (1926).

[44] Katz, *Kolloidchem. Beihefte*, **9**, 1 (1917).

[45] Ostwald, *Kolloid-Z.*, **49**, 60 (1929).

[46] Freundlich and Posnjak, *Kolloidchem. Beihefte*, **3**, 417 (1912); Bary, *Compt. rend.*, **170**, 1388 (1920).

[47] Fikentscher and Mark, *Kolloid-Z.*, **49**, 135 (1929).

[48] Staudinger and Heuer, *Ber.*, **63**, 2933 (1929).

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Isoprene and Rubber

Part 21.[1] The Molecular Size of Rubber and the Nature of Its Colloidal Solutions

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FREIBURG, I.B.

I. The Significance of Studies of the Model

In an address at last year's general meeting at Hanover,[2] I discussed the experimental evidence which led me to the hypothesis that rubber consists of extraordinarily large molecules, and that in a diluted colloidal rubber solution the primary colloidal particles are identical with the molecules, that the rubber is therefore built up from macromolecules. The evidence is based on experiments on synthetic substances, chiefly on studies on polysterols.[3] Furthermore, the transformations of rubber indicate that it is a very high molecular substance according to the old concepts,[4] as shown for example in the conversion of rubber into colloidal soluble hydrorubber[5] and in the irreversible breaking down of rubber at higher temperatures, which indicate a cracking of the large molecules. In these studies the molecular size was determined chiefly by viscosity measurements,[6] because numerous studies, principally on synthetic substances, have shown that in a series of homologous polymeric products of equal concentration the higher molecular product has solutions of higher viscosity than the product with lower average molecular weight. Studies in viscosity have already led to the idea that in rubber there must be a very high molecular substance of an average molecular weight of 100,000.

Therefore the investigations on the model of polysterols are of fundamental importance in the research on the constitution of rubber, and without the exact knowledge of the polysterols it would not have been possible to explain the nature of rubber. Apparently the hard, viscous, glass-like polysterol[7] has nothing in common with rubber. Heated to 100°, however, it becomes elastic and very similar to rubber. At ordinary temperatures, therefore, the polysterol resembles a frozen rubber.[8] In contrast to this, it has the advantage over rubber of great stability, since it has a saturated hydrocarbon chain corresponding to the following formula

$$CHRCH_2(CHRCH_2)_x\ CHRCH_2, \text{ where } R = C_6H_5 \text{ and } x = 2 \text{ to } 1000.$$

With the polysterol it is not necessary to work in the absence of air. Therefore the relations between molecular weight and viscosity were discovered first in the case of polysterols on account of their stability. Viscosity measurements on rubber solutions give useful results only if carried out with complete exclusion of air.

II. Micelle or Macromolecule in a Rubber Solution

As is known, during the last decades, with the application of principles of colloid chemistry, a micellar structure[9] has been attributed to the rubber particle in solution. Thus Pummerer in particular defends this structural concept of the rubber particle.[10] Recently Meyer and Mark, endeavored in a very interesting way to bring the observations of Pummerer into agreement with the earlier ideas, according to which rubber was assumed to be a very high molecular substance. They assume that rubber is composed of micelles which produce a bundle of shorter high valence chains. In order to further characterize the concept of these authors a quotation from one of their publications is given.[11]

The high viscosity of these solutions, for example in benzene, permits the conclusion that very large highly solvated micelles exist in this solvent. On the other hand, the well-known experiments by Pummerer[12] on the "molecular weight" of rubber in camphor and menthol indicate that under the influence of certain solvents the micelles disassociate either into smaller aggregates of high valence chains or into high valence chains themselves. According to this point of view, rubber would occupy a middle position between soap solutions, whose molecules are found in a permanent equilibrium with free fatty-acid molecules, and cellulose or starch, where the micelles cannot be split up reversibly by any solvent.

The so-called technical effect of the mechanical "dead milling" and "recovery" of rubber indicate that a very slowly appearing equilibrium determines the conditions. We can also regard as micelles of various particle size the fractions termed by Pummerer sol- and gel-rubber, whose chemical composition and x-ray diagram are completely identical.

On the basis of osmotic determinations in benzene solution, the molecular weight was not determined[13] by these authors but rather the micelle weight. According to my concept, on the contrary, macromolecules and not micelles are present[14] in a very dilute rubber solution, and Wolfgang Ostwald[15] has recently confirmed this observation in a very interesting work in which he recalculated the osmotic determinations of Caspari.[16]

With polysterol solutions it could be proved beyond objection that macromolecules and not micelles are present in dilute solutions, since the relative viscosity of this solution does not change with increase in temperature, but remains the same even after repeated cooling and heating of the solution.[17] The relative viscosity would, however, change with such a treatment of the solution if micelles were present in it, because these would dissolve more or less with rise in temperature and this would make itself evident by changes in the viscosity. This is not the case with dilute solutions. Only in the case of concentrated solutions, in which "colony formation" is already present have changes in the relative viscosity been observed with temperature variations.

It was also possible to prove the existence of macromolecules in solution in the case of balata and rubber. Here such a proof is much more difficult, since all the oxygen must be removed from the solvent with the greatest of care.[18]

III. The Molecular Weight of Rubber[19]

Studies in viscosity offer a new way to determine the size of the rubber molecule. In earlier work[20] it was shown that a relation exists between the molecular weight and the viscosity of solutions of equal concentration in a homologous polymeric series. The results were not evaluated quantitatively earlier because difficulties were met in these experiments.[21] With such high polymeric substances it is not a question of products made up of molecules of uniform size, but instead of a mixture of homologous polymeric products. They are therefore true molecules of the same structural principle, although of various degrees of polymerization.[22] For the first time it was possible to prove that with well-fractionated mixtures of polysterols there is a very simple quantitative relation between the viscosity of solution and the molecular weight, if the specific viscosity[23] of a solution is calculated. This is a new figure of unusual importance in viscosity studies and is obtained from the Einstein formula:

$$\eta_r - 1 = \eta_{sp}$$

The increase in viscosity produced in a solvent by a dissolved substance is physical. According to the well-known Einstein viscosity formula $\eta_r = 1 + K\phi$, therefore $\eta_{sp} = K\phi$. The specific viscosity of solutions of the same concentration should be independent of the degree of dispersion of the dissolved substance. This is the case for example with suspensions.[24] A 1% rubber solution should, therefore, always

show the same viscosity, whether broken-down rubber or rubber not broken down is dissolved. Actually the differences are extraordinarily great. 1% solutions of rubber not broken down show, according to the type, specific viscosities η_{sp} of 5 to 20, and have therefore a very high viscosity. 1% solutions of highly broken down semi-colloidal rubber have η_{sp} of 0.1 to 0.5. In other words, such solutions are scarcely more viscous than the solvent. Here, therefore, contrary to the Einstein law, the degree of dispersion, *i. e.*, the length of the molecule, has a decisive influence on the viscosity.

With synthetic products, for example, polysterols, there is a simple relation, namely, that the specific viscosity of solutions of the same concentration increases in proportion to the molecular weight so that the following equation applies

$$\eta_{sp} = K_m M c^{25}.$$

On this basis K_m is called the viscosity-molecular weight constant. Such a relation between viscosity and molecular weight permits the calculation of semi-colloidal decomposition products of rubber and gutta-percha, and on the basis of the following classification a constant of 0.3×10^3 was obtained for four polyprenes of different molecular weights.

TABLE I

Substance	Molecular Weight in Benzene	Relative Viscosity $\eta_r = \eta_c/\eta^L$ of a 0.25-Molar Soln. in Benzene	Specific Viscosity $\eta_{sp} = (\eta_r - 1)$	η_{sp}/C	$K_m = \frac{\eta_{sp}}{cM} \times 10^3$
Rubber broken down in tetralin	3400	1.263	0.263	1.052	0.31
Rubber broken down in xylene	4250	1.285	0.285	1.140	0.27
Gutta-percha broken down in tetralin	6400	1.507	0.507	2.028	0.32
Gutta-percha broken down in xylene	2700	1.200	0.200	0.800	0.30

In an earlier work,[26] a large number of cyclo rubbers and cyclo gutta-perchas were prepared as decomposition products of rubber and gutta-percha, respectively. As the following Table IA shows, the constant K_m varies greatly with these cyclo rubbers and cyclo gutta-perchas. Moreover, in every case the constant is smaller than that calculated in Table I from rubber and gutta-percha. The latter fact is not surprising, because cyclo rubbers belong to another homologous polymeric series than the polyprenes. Furthermore, cyclo rubbers and cyclo gutta-perchas are not simple polymers, but they can be more or less cyclicized. This explains also the fluctuating values of K_m in Table IA.

TABLE IA

Substance	Molecular Weight in Benzene	Relative Viscosity $\eta_r = \eta_c/\eta^L$ of a 0.25-Molar Soln. in Benzene	Specific Viscosity $\eta_{sp} = (\eta_r - 1)$	η_{sp}/C	$K_m = \frac{\eta_{sp}}{cM} \times 10^3$
Cyclo rubber broken down in tetralin	2,500	1.15	0.15	0.60	0.24
Cyclo gutta-percha broken down in tetralin	2,500	1.15	0.15	0.60	0.24
Cyclo rubber broken down in xylene unfractionated	8,100	1.265	0.265	1.06	0.13
Cyclo gutta-percha broken down in xylene unfractionated	3,400	1.18	0.18	0.72	0.21
Cyclo rubber broken down in xylene ether-soluble	4,600	1.17	0.17	0.68	0.15

Cyclo rubber broken down in xylene insoluble in ether	12,000	1.33	0.33	1.32	0.11
Cyclo gutta-percha broken down in xylene soluble in ether	2,700	1.17	0.17	0.68	0.25
Cyclo gutta-percha broken down in xylene insoluble in ether	7,600	1.26	0.26	1.04	0.14
Cyclo rubber broken down in toluene unfractionated	13,000	1.26	0.26	1.04	0.08
Cyclo gutta-percha broken down in toluene unfractionated	10,000	1.21	0.21	0.84	0.084

Suppose now that the relations between viscosity and molecular weight in the case of semi-colloidal decomposition products are also valid for eucolloidal rubber and balata, then, on the basis of viscosity determinations of very dilute solutions[27] the molecular weight can be calculated and the values in Table II are obtained.

TABLE II

Substance	Viscosity Measured in Molarity	η_{sp}	$\frac{\eta_{sp}}{c}$	$M=\frac{\eta_{sp}}{cK_m}$ $K_m=0.3\times10^{-3}$	$m=K_c\times10^3$
Raw Hevea rubber	0.0125	0.68	54.9	180,000	160,000
Rubber purified according to Pummerer:					
Difficultly soluble	0.025	0.543	21.8	73,000	77,000
Easily soluble	0.025	0.389	15.5	52,000	56,000
Balata	0.025	0.386	15.4	51,000	52,000
Masticated rubber	0.025	0.19	7.6	25,000	30,000

There is a very high molecular substance in rubber purified by the Pummerer method.[28] Corresponding to our first hypothesis, there are in one macromolecule approximately 1000 base molecules united in a long chain. The primary colloid particles which, according to the above reasoning, produce molecules, possess, therefore, an astonishingly high molecular weight. One rubber molecule is accordingly comparable to a very long slender thread. The diameter of such a molecule is from 2 to 4 Å. U. and therefore has molecular dimensions. The length may on the contrary be from 2000 to 4000 Å. U., according as to whether it is a thread or a ring (a double thread). The macromolecule reaches in one dimension, its length, almost to the wave-length of visible light itself, and therefore has in one direction the dimensions of a colloid. In spite of this, these molecules are not visible because the breadth and thickness of such a molecule are too small.

The objection can be raised that in this determination of the size of the rubber molecule the relations between viscosity and molecular weight, as have been found for semi-colloids, are not valid for eucolloids. However, if the changes in properties of individual members of homologous polymeric series with increasing degrees of polymerization are considered, then one is led to this high molecular size of eucolloids. This is especially the case with the homologous polymeric series of polysterols.[29] Furthermore, polyprenes still have a semi-colloidal character at a molecular weight of 6800, or a degree of polymerization of 100, dissolve without swelling, and their solutions are of low viscosity. Therefore one cannot ascribe to the rubber molecule the approximate magnitude of $(C_5H_8)_8$ as Pummerer has assumed for his part, nor is it possible that the high valence chain of rubber has a magnitude of from $(C_5H_8)_{100}$ to $(C_5H_8)_{150}$, corresponding to the data of Mark and Meyer,[30] for this would be at variance with all experiments on homologous polymeric series, since hydrocarbons of this order of magnitude have semi-colloidal properties.[31] Finally the determinations of Wo. Ostwald,[32] who used the osmotic determinations of Caspari, lead to the same order of magnitude for the rubber and balata molecule.

Based on other considerations, relations can be proved between viscosity and

molecular weight. As far as is known, the viscosity of a solution does not change in proportion to increasing concentration as one is led to expect from the Einstein law, but increases much more strongly, and the larger the molecules in solution the greater is the increase, as the accompanying curves show. There the relative viscosity is given of three semi-colloidal polyprenes of a molecular weight of 2400, 4200 and 6500 at different concentrations, and for comparison with this that of of balata of molecular weight of 51,000 and of rubber purified according to the method of Pummerer having a molecular weight of 77,000.

According to investigations by Arrhenius[33] and Duclaux[34] this increase in viscosity can be expressed in the following relations

$$\eta_r = 10^{kc} \quad \text{or} \quad K = \log \eta_r / c$$

If this constant K_c which is termed the viscosity-concentration constant, is determined for various semi-colloidal polyprenes of known molecular weight, then a simple relation between this constant and the molecular weight [35] is obtained in an approximate way. The molecular weight is $M = K_c 10^4$. If one now determines the viscosity-concentration constant for rubber and balata (products of uncertain molecular weight), and assumes on the basis of the properties of homologous polymeric series that these relations obtained for semi-colloids are also valid for eucolloids, then one obtains as shown in Table II, approximately the same values for the molecular weight as those based on calculations of the viscosity-molecular weight constant.

The order of magnitude of the molecular weight of rubber, gutta-percha, and balata is therefore fixed, and we have to deal with the remarkable fact that in solutions of these substances extraordinarily long molecules, or macromolecules, are present. These are very sensitive, are easily oxidized and cracked, which can be most easily observed in the great diminution of the viscosity of their solutions. Viscosity determinations will therefore play an important part in rubber chemistry in the future in the investigation of the chemical changes in the sensitive rubber molecule.[36]

IV. The Nature of the Colloid Solution

In the preceding section it is proved that extraordinarily long molecules are present in a rubber solution. An homologous polymeric series of polyprenes exists, of which the lower semi-colloidal members have properties like simple organic compounds. Proof that rubber itself differs from the low molecular polyprenes solely in its molecular size still does not explain its peculiar behavior in solution. This consists in the fact that rubber swells greatly in organic solvents, while low molecular substances dissolve without swelling. Furthermore, a very dilute, *i. e.*, a 1% rubber solution, is highly viscous, while a 1% solution of a low molecular polyprene shows a viscosity scarcely greater than that of the solvent. In the case of a rubber solution, the viscosity does not increase in proportion to increase in concentration, but very much more rapidly, whereas with a solution of a low molecular substance the viscosity does not increase abnormally with increasing concentration.

These very considerable differences shown by rubber in contrast to low molecular substances, are the reasons for ascribing an entirely different structure to this and other high molecular substances. They lead to the assumption that these substances possess a micellar structure, and that the surprising properties of rubber in solution depend upon a high solvation of these micelles (see the views of Meyer and Mark). This assumption, as was discussed above, is not correct, and it will be shown below that the colloidal nature of the rubber solution may be explained in a simple way by its synthesis from macromolecules.

The field of action of such a thread-like molecule, or the volume occupied by a molecule in a liquid does not increase in proportion to the specific volume of the molecule, but is much greater and indeed is proportional to the square of the length of the molecule. This fact results from the foregoing relations between the viscosity and molecular weight. Attention should be called to the fact that according to the Einstein law the specific viscosity should be independent of the degree of dispersion, therefore it should satisfy the equation $\eta_{sp} = Kc$. Actually, however, investigations of semi-colloidal products give the formula

$$\eta_{sp} = KcM.$$

therefore the viscosity is proportional to the length of the molecules. This relation shows, as was derived elsewhere,[37] that the volume of the molecule corresponds to the square of its length. In order to make this result clear one must imagine that a molecule is not fixed in the liquid, but that it oscillates in different directions. The sum of the movements made by such a molecule represent the field of action of the molecule, and this field of action is represented by the volume of a short cylinder which is described in the rotation of the molecule.

If now we consider a 0.1-molar solution of various homologous polymeric polyprenes, that of semi-colloidal decomposition products of balata and rubber, then the number of molecules is quite different in this 0.68% solution. The number is small if the molecules are very large and *vice versa*, and indeed the number of molecules diminishes in proportion to the molecular size. The field of action of the molecule, however, does not increase in proportion to the length of the molecule, but as discussed above it is proportional to the square of the length. From this is derived the additional fact that the total field of action of the numerous small molecules of a semi-colloidal polyprene is smaller than that of a few large molecules. If one calculates this total field of action, as shown in the following table, the astonishing fact appears that a 0.1-molar solution of a rubber of a degree of polymerization of 1000, that is, of a molecular weight of 68,000, requires a greater volume than the volume available. Therefore, because of their great space requirements, the relatively few molecules in this very dilute solution can find no room; they interfere with one another and are no longer normally dissolved. Only in a 0.067-molar solution of this rubber, that is, a 0.46% solution, is the field of action as large as the volume available. Still more dilute solutions must be prepared if the molecules are to move as freely as in a dilute solution of a low molecular substance.

Table III shows further that in a 0.1-molar semi-colloidal solution the total field of action of the dissolved molecules is much less than that of the available volume, and in fact is only 15% of this volume. The field of action of the molecule in the case of low molecular polyprenes of a degree of polymerization of 10 in a 0.1-molar solution is very small, being only 1.5% of the total volume. Here, therefore, the molecules move freely, and such a solution behaves in a completely normal manner. The remarkable fact is to be noted that in a one to five per cent rubber solution, such as has been generally used up to now in investigations, the rubber molecules not normally dissolved are in such a state that they move freely. In this solution we have a peculiar state of solution for which the term *gel-solution* is proposed. These gel-solutions in which the molecules interefere with one another usually pass over to the true gels in which the solvent has penetrated between the large molecules and the molecules themselves no longer possess free movement. The field of action of this molecule is then too great in comparison with the space at its disposal. If one tries to dissolve 1 mol of rubber,[38] *i. e.*, 68 g. in a liter, no solution is obtained, but only a swelling that is a gel. The field of action of the rubber molecule is 15% greater for a molecular weight of 68,000 than the volume available.

Therefore fifteen times as much solvent would have to be added in order to reach the limit of the normal solubility or the dilution at which all the large molecules move freely. A solution in which such a free movement of the large molecules exists is termed a sol-solution; only solutions of such concentration are comparable to those of low molecular substances. The viscosity-molecular weight constant can be determined only in sol-solutions. Likewise osmotic determinations lead to the correct values for the molecular weight only with this type of solution.

It is therefore comprehensible that low molecular substances dissolve in a normal way, without swelling, while high molecular substances swell first and then dissolve. The addition of a small quantity of solvent is sufficient to produce a normal solution with low molecular substances. With high molecular substances on the contrary one obtains gel-solutions or gels if not very large quantities of solvent are employed, since the solvent is not sufficient for the formation of a sol-solution, or the true solution.

Summarizing the essential points once more, the peculiar behavior of a rubber solution, *e. g.*, its high viscosity, depends upon the fact that for the most part gel solutions are present, that is, solutions in which the large molecules have insufficient space. Special hypotheses such as the formation of micelles and strong solvation of these micelles are not necessary to explain the nature of these colloidal solutions. We have rather, as has already been emphasized in earlier work, in all properties a gradual transition of low molecular substances to high molecular ones, and the special behavior of the latter depends on the length of their molecules.

References

[1] 20th Communication, *Ber.*, **63**, 921 (1930).

[2] *Kautschuk*, Aug.-Sept., **1925**; **1927**, 63; **5**, 94, 161 (1929).

[3] Staudinger, Brunner, Frey, Garbach, Signer and Wehrli, *Ber.*, **62**, 241 (1929); Staudinger and Frey, *Ibid.*, **62**, 2909 (1929).

[4] Weber, *Ibid.*, **33**, 789 (1900).

[5] Staudinger and Fritschi, *Helvetica chim. acta*, **5**, 787 (1922).

[6] Staudinger and Bondy, *Ann.*, **468**, 1 (1929); Staudinger, *Ber.*, **59**, 3031 (1926).

[7] *Ber.*, **62**, 242 (1929).

[8] Hock, *Z. Elektrochem.*, **31**, 407 (1925); *Kautschuk*, **1930**, 470.

[9] The same views now appear in textbooks, *e. g.*, *Organische Chemie* (by Oppenheimer), 2nd Ed., p. 327.

[10] *Handbuch der Kautschukwissenschaft*, 257; *Kautschuk*, **5**, 129 (1929).

[11] Meyer and Mark, *Ber.*, **61**, 1945 (1928). In a recent publication Fikentscher and Mark forsake this view and adopt the views of the author of the present paper. They assume that in a solution rubber is dissolved in the molecular state, and that rubber and its decomposition products form a polymeric homologous series. It is therefore assumed that in the decomposition the large rubber molecules are cracked and not a solution of micelles, a view which is taken by Staudinger and Bondy (cf. *Ann.*, **468**, 1 (1929)).

[12] Note cited: "Of course the low experimental values of Pummerer (average molecular weight approximately 1000) seem to us too low. Even if all micelles are decomposed completely into primary valence chains, an average molecular weight over 5000 should be expected. Perhaps on heating in camphor or menthol ether there is a cracking of the chains, and then again the phenomenon may be influenced by small quantities of non-rubber substances."

[13] Kroepelin and Brumshagen, *Ber.*, **61**, 2441 (1928).

[14] Staudinger and Fritschi, *Helvetica chim. acta*, **5**, 785 (1922).

[15] Wo. Ostwald, *Kolloid-Z.*, **49**, 60 (1929).

[16] Caspari, *J. Chem. Soc.*, **105**, 2139 (1914).

[17] Staudinger and Heuer, *Ber.*, **62**, 2933 (1929).

[18] Staudinger and Leopold, *Ber.*, **63**, 730 (1930). Similar investigations on rubber have been undertaken by Bondy but have not yet been published.

[19] Staudinger and Bondy, *Ber.*, **63**, 734, 921 (1930).

[20] Staudinger, *Ber.*, **59**, 3031 (1926).

[21] *Helvetica chim. acta*, **12**, 942 (1929).

[22] Staudinger, *Z. angew. Chem.*, **42**, 69 (1929).

[23] Staudinger and Heuer, *Ber.*, **63**, 222 (1930).

[24] Bancelin, *Compt. rend.*, **152**, 1382 (1911).

[25] Staudinger and Heuer, *Ber.*, **63**, 222 (1930); Staudinger and Heuer, *Ber.*, **63**, 222 (1930); Staudinger, *Kolloid-Z.*, **51**, 71 (1930).

[26] *Ann.*, **468**, 1 (1929).

[27] The measurements must be carried out within the range of sol. solutions. See last diagram.

[28] Pummerer, Andriessen, and Gündel, *Ber.*, **61**, 1583 (1928).

[29] *Ber.*, **62**, 241 (1929).

[30] *Ber.*, **61**, 1945 (1928); Meyer, *Z. angew. Chem.*, **41**, 935 (1928).

[31] *Ber.*, **62**, 241 (1929); *Helvetica chim. acta*, **12**, 934 (1929).

[32] *Kolloid-Z.*, **49**, 60 (1929).

[33] Arrhenius, *Biochem. J.*, **11**, 112 (1927).

[34] Duclaux and Wollmann, *Bull. soc. chim.* [4], **27**, 414 (1920).

[35] Staudinger, *Ber.*, **63**, 921 (1930); *Kolloid-Z.*, **51**, 80 (1930).

[36] Staudinger and Leopold, *Ber.*, **63**, 732 (1930).

[37] Staudinger, *Kolloid-Z.*, **51**, 80 (1930); *Ber.*, **63**, 929 (1930).

[38] Here as in all previous cases, a base molecule of C_5H_8 was considered to be 1 mol.

[39] Cf. Ostwald's calculations. The limiting values of the osmotic pressure at great dilution, *i. e.*, within the range of sol solution, serve for the calculation of the molecular weight of rubber *Kolloid-Z.*, **49**, 60 (1929).

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An Investigation of the Viscosity of Rubber Solutions

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Viscosity measurements have frequently been made with rubber, and very many suggestions have been put forward to explain the cause of the changes of viscosity in rubber solutions. According to Staudinger (*Kautschuk*, **5,** 128 (1929)), if measured under certain conditions, *e. g.*, in dilute solutions where no irregularities are found, the viscosity can be used as a measure of the molecular weight of the dissolved substance. Fickentscher and Mark (*Kolloid-Z.*, **49,** 140 (1929)) even calculate from viscosity measurements the length of the molecule and hence relative molecular weights.

It is well known that the viscosities of rubber solutions differ greatly and that mechanical treatment of the rubber decreases the viscosity of its solutions to a very large extent. The latter effect has been explained by Staudinger as well as by Fickentscher and Mark (*loc. cit.*) as a depolymerization. The latter authors calculate that the molecular weight of rubber decreases to one-third of the original if it is masticated for 225 minutes.

It has further been pointed out recently by Herschel and Bulkley (*Kolloid-Z.*, **39,** 291 (1926)) that rubber solutions show irregularities in their viscosity, *e. g.*, the viscosity is not linearly proportional to the pressure. (According to Poiseuille's formula for the rate of flow of a liquid through a capillary, the viscosity coefficient:

$$\eta = \frac{\pi P.R.^4T.}{8L.Q.}$$

where R and L are the radius and length of the capillary, respectively, and Q is the volume of liquid discharged in time T under a pressure of P. If R, L, and Q are constant then η should be proportional to the product of P and T.) This deviation from Poiseuille's law has been found frequently in colloidal solutions and has been given the name "structure viscosity." These authors worked out a formula for this magnitude on an empirical basis similar to that suggested by several other authors. They further found that rubber solutions exhibit thixotropy, *i. e.*, change of consistency on mechanical treatment.

In connection with the conclusions about the molecular weight of rubber, and especially the explanation of the process of mastication, it must be mentioned that Stamberger (*J. Chem. Soc.*, **1929,** 2318) found no difference in the vapor pressure lowering between over-masticated and unmasticated rubber. The latter result makes it seem highly improbable that changes in viscosity and molecular weight are related.

In the present investigation it will be shown that the viscosities of rubber solutions are increased if a highly active filler, *e. g.*, carbon black is incorporated in the rubber. Polymerization seems to be very improbable, since the rubber if separated from the carbon black, has the original viscosity.

Twiss (*J. Soc. Chem. Ind.*, **44,** 106T (1925)) and other authors (M. Le Blanc, Kröger & Kloz, *Kolloidchem. Beihefte*, **20,** 356 (1925)) have mentioned that rubber-carbon black mixes do not dissolve, but only show swelling similar to that exhibited by vulcanized rubber. It has, however, been found possible to dissolve these mixes. The method adopted for their investigation was the following:

(1) Pale crepe was over-masticated on cold rolls for 8–10 hours.
(2) Mixes containing 2½, 5, 7½, 10, and 15 per cent. by weight, of carbon black were made from the above over-masticated rubber. A standard carbon black, "Micronex," was used.
(3) Solutions of these mixes in benzene were made within five minutes of mastication. The concentration being adjusted to 10 gms. of rubber per 100 cc. of solution. The viscosities of these solutions were determined within 24 hours.
(4) Identical sets of solutions were made up four days after the mastication process, and the viscosities were measured.
(5) This was repeated thirty days after mastication. In every case the mix dissolved with the exception of that containing 15 per cent. of carbon black that had stood thirty days; this swelled to a homogeneous jelly.

The viscosity measurements were made at constant temperature (25° C.), using two Ostwald viscometers with a mean head of liquid corresponding to about 8 cm. of water. The variation of viscosity with pressure was also investigated. The arrangement was similar to that used by Applebey; here a viscometer of the Bingham type was employed (Hatschek, *Viscosity of Liquids*, **1928,** 41 and 44).

The dimensions of the capillaries of the viscometers are given below:

(*a*) Ostwald 1 length 7.5 cm. diameter 0.72 mm.
Ostwald 2 length 7.5 cm. diameter 1.02 mm.
Bingham length 5.0 cm. diameter 0.72 mm.

The relative viscosities (benzene = 1), determined in the Ostwald viscometers at constant pressure, of the solutions made up from the mixes immediately after mastication, four days after mastication and 30 days after mastication are given in Table I.

TABLE I

IMMEDIATELY AFTER MASTICATION

Per Cent. Concentration of Solution	Per Cent. of Carbon Black in Mix. 0	2½	5	7½	10	15
2½	7.02	4.64	5.25(?)	5.15	6.86	7.75
5	19.30	12.80	14.30	16.20	17.90	21.40
7½	56.30	32.20	35.20	38.00	47.50	62.30
10	141.00	68.30	86.00	95.00	105.00	148.00

AFTER 4 DAYS' STANDING

Per Cent. Concentration of Solution	Per cent. of Carbon Black in Mix. 0	2½	5	7½	10	15
2½	6.88	...	4.90	5.45	6.10	8.10
5	19.50	...	16.50	17.20	18.50	22.50
7½	55.10	...	42.30	46.30	56.50	68.00
10	143.00	...	96.00	105.00	135.00	230.00

AFTER 30 DAYS' STANDING

Per Cent. Concentration of Solution	Per cent. of Carbon Black in Mix. 0	2½	5	7½	10	15
2½	....	4.62	4.95	6.20	....	8.50
5	....	14.20	18.80	20.00	....	25.40
7½	....	38.80	50.90	54.00	....	69.50
10	....	97.00	125.00	140.00	....	257.00

It will be seen that there is an increase of viscosity with increasing carbon black content and with increasing time of standing of the undissolved mixes.

The results given in the first column in each case refer to a sample of over-

masticated rubber taken from the batch into which the carbon black was afterward mixed. The process of mixing the carbon black into the rubber would probably account for the mixes giving lower viscosities than the over-masticated rubber. Also mastication would be more effective on account of the additional shearing produced by the carbon black. A further 20–25 minutes' mastication of the rubber lowered the viscosity of a 10 per cent. solution to approximately 100.

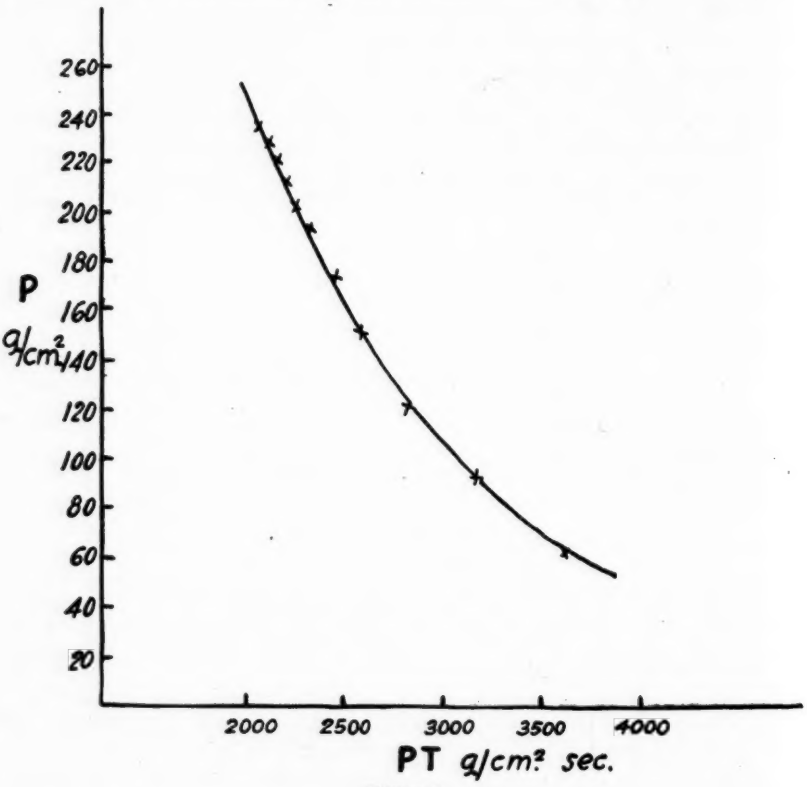

Figure 1

All the above values were obtained after shaking the solutions. It was found that in some cases if the solutions were not shaken their viscosities decreased, as the liquid was repeatedly passed through the capillary, to a final value which is that obtained by shaking the solutions. This behavior is called thixotropy. A few typical results are given in Table 2. Here it must be emphasized that the mix containing 15 per cent. of carbon black that swelled to a jelly could be liquefied by vigorous shaking.

TABLE II

Solution	Before Shaking	After Shaking
(AFTER 4 DAYS' STANDING)		
10 %; 7½% carbon black ..	113.00	105.00
7½%; 10 % carbon black ..	59.30	56.50
7½%; 15 % carbon black ..	92.50	68.00
10 %; 15 % carbon black ..	310.00	230.00

(After 30 Days' Standing)

10 %	$2^1/_2$% carbon black ..	102.00	95.00
	$7^1/_2$% carbon black ..	152.00	140.00
	10 % carbon black ..	186.00	150.00
	15 % carbon black ..	jelly	257.00

The results obtained by Herschel and Bulkley (*loc. cit.*) for the variation of viscosity with pressure in the case of 1.21 per cent. solution of unmasticated rubber

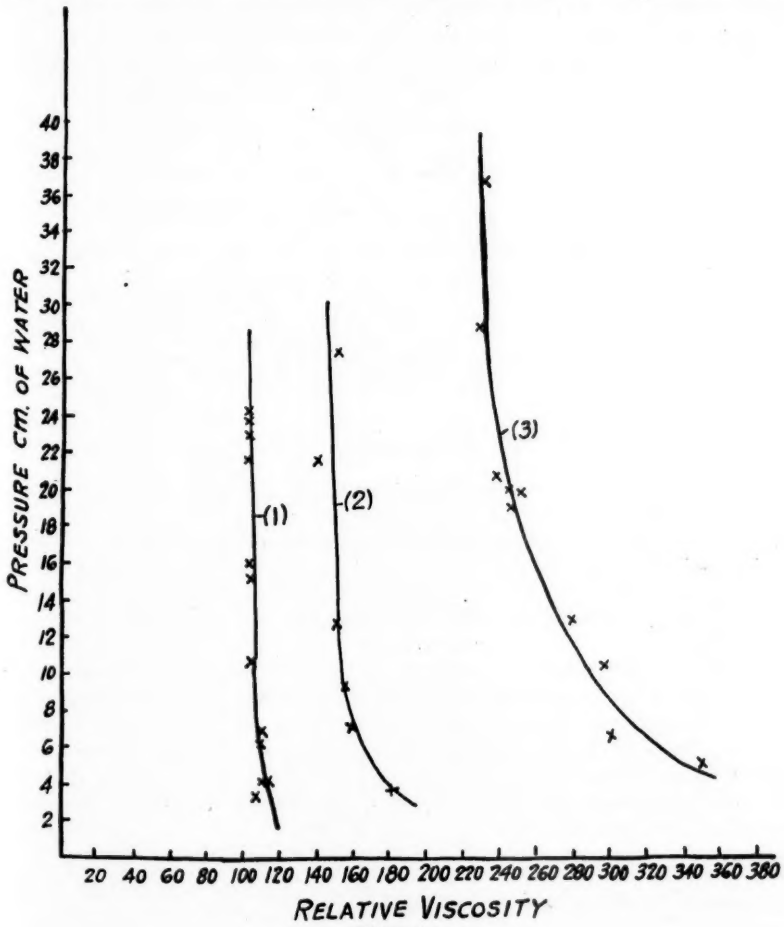

Figure 2

are given in Fig. 1. The ordinates are pressures in g./cm.^{2}, the abscissae the products of pressure and time (in seconds) taken to discharge a given volume of liquid. The results obtained for over-masticated rubber and carbon black mixes are shown in Fig. 2; the ordinates here being pressures (in cm. of water) and the abscissae relative viscosities; *i. e.*, P_sT_s/P_oT_o, where T_s is the time (in minutes) taken to discharge a given volume of solution under a pressure of P_s, and P_o and T_o are the corresponding values for benzene. P_oT_o is naturally a constant. Curve (1)

is that obtained for a 10 per cent. solution of over-masticated rubber, and curves (2) and (3) for 10 per cent. solutions of carbon black mixes, containing 10 and 15 per cent. of carbon black, respectively, that had stood for thirty days. It is seen that structure viscosity is very slight indeed in the case of the over-masticated rubber and becomes very marked in the case of the carbon black mixes. (It was thought convenient not to use the formulae for structure viscosity which have been put forward as there is not one that is generally accepted. The results are given in a simple way so that it is possible to calculate this value on the basis of any desired formula.)

The phenomena of the so-called structure viscosity and thixotropy are generally explained by assuming the presence of a structure in the solution, which produces the elasticity observable in it. Nearly all jellies show this behavior. In many cases this structure can be destroyed by slight mechanical treatment only, when the consistency changes from a solid to a liquid. It has been shown that solutions of over-masticated rubber do not show marked structure viscosity, *i. e.*, they are structureless. Mastication, therefore, seems to be the breaking down of a structure, as suggested by Klein and Stamberger (*Kolloid-Z.*, **35,** 362 (1924)).

On the addition of carbon black, a structure is built up again to a certain extent and the viscosity, elasticity, and structure viscosity increased. This effect, moreover, increases with time and can be reversed by remastication. The formation of this structure can be explained on the basis of the suggestion of McBain (*J. Am. Chem. Soc.*, **49,** 2230 (1927)) that an orientation of the rubber particles takes place on the carbon black particles. The fact that the process is slow lends support to this theory.

Conclusions

1. It has been shown that solutions of over-masticated rubber show small structure viscosity.
2. The viscosity of solutions of this rubber mixed with carbon black increases with increasing carbon black content. These solutions show structure viscosity as well as thixotropy. The values increase with the time of standing.
3. The rubber that diffuses out of those mixes that only swell to a jelly has the original viscosity.
4. From this behavior it is concluded that the viscosity of rubber solutions bears no relation to the molecular weight of the rubber and that mastication is not a process of depolymerization as suggested by several authors.
5. The changes can be explained sufficiently well by assuming that a structure is destroyed and built up again.

The author expresses his thanks to Dr. P. Stamberger for his help and advice throughout this investigation.

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Discussion

T. J. Drakeley asked if Blow had tried any method other than Poiseuille's for determining viscosity, as the method and formula were not always applicable to materials of a plastic nature. He also drew Blow's attention to an apparent contradiction, for in the paper it was stated that carbon black tended to build up the structure of the rubber, whereas it was also a conclusion that the rubber which diffused from a carbon black mix had the original viscosity. If the carbon black

built up the structure, surely the viscosity of the rubber from such a mix would be higher than its original value.

De Waele said he believed that Herschel, in his papers on the viscosity of rubber sols, had established that "structure viscosity" could be shown in the rubber sol itself when pigments were absent. The lowest concentration examined was 0.2 per cent., and he had worked up to about 1.5 per cent., structure viscosity being shown only in the higher concentrations. One wished that Blow had carried out his viscosity determinations with a variable pressure viscometer in order to permit a closer analysis of his results. While a number of workers on colloidal systems have noted variation of viscosity with the rate of shear, as distinct from the constancy of viscosity under the same conditions obtaining with true fluids, an interpretation of the manner of the said variation of viscosity has been proposed by Bingham, who formulated the equation:

$$\frac{P - f}{V} = \eta \tag{1}$$

which is comparable to the equation of flow for a true fluid:

$$\frac{P}{V} = \eta \tag{2}$$

where P is the shearing force, V the rate of shear and η the viscosity.

Bingham's equation, while representative of a system showing variation of viscosity with rate of shear, and comprising a "rigidity" or "yield-value" term f characterizing the "stay-puttedness" of the material, has been criticized by a number of workers on the score of its inadequacy to represent the dynamic behavior of many systems showing a departure from Poiseuille's equation of flow for a true fluid. Thus, the present author in 1923 proposed the formula:

$$\frac{P}{V\phi} = \eta \tag{3}$$

where ϕ is a fractional exponent characteristic of each material, as representing the stress/shear behavior of non-homogeneous systems *at a sufficiently high rate of shear*. Equation (3) again is representative of variation of viscosity with rate of shear, the relationship of the variables being parabolic, as distinct from Bingham's earlier conclusion as to a hyperbolic relationship.

However, Equation (3) does not give an idea of the "stay-put" property of certain colloidal systems, *e. g.*, the gels referred to in the present paper, and in order to express mathematically the semi-solid nature of such bodies a rigidity term needs to be introduced. Both Herschel and the speaker have independently proposed somewhat similar formulae to express the anomalous behavior of the substances dealt with in the present paper:

$$\frac{P - K}{V\phi} = \eta \text{ (Herschel)} \tag{4}$$

$$\frac{P - fe^{-\text{shear}}}{V\phi} = \eta \text{ (de Waele)} \tag{5}$$

where K and f in the respective formulae are characteristic of rigidities. While Herschel, however, assumes rigidity to be constant at all rates of shear, de Waele claims that the *virtual* rigidity forming the second term varies inversely with the rate of shear (e = log base). While the speaker merely indicates that a further equation has been proposed to show the rate of regain of rigidity at rest after shear, it is merely necessary to state that the liquifaction of a gel on agitation and its subsequent gelation at rest is covered by such formulae.

While the K and f terms in Equations (4) and (5), respectively, permit one to follow the growth of rigidity over a series at, *e. g.*, increasing concentration of disperse phase, the exponent ϕ although not characterizing any outward or tangible property, has been claimed by de Waele and Lewis (*Kolloid-Z.*, **48**, 126 (1929)) to characterize the degree of lyosorption of the disperse phase in the system.

The author would, therefore, conclude that by a closer analysis of the stress-shear figures than is afforded by mere expression of viscosity at differing rates of shear, more illuminating interpretations might be obtained from the experiments on the addition of carbon black to the rubber mixes.

Stamberger said that the mathematical formulae derived by de Waele for solutions showing variation of viscosity coefficient with variation of pressure were mainly on an empirical basis. The formula of Herschel and Bulkley was derived on just as much an empirical basis as Bingham's formula. These formulae are not generally accepted and are still open for criticism. He considered that Blow had done well in giving his results in a simple way instead of choosing one of the complicated formulae.

A. de Waele said it might be replied to Stamberger's accusation as to the "empirical" nature of the flow formula referred to, that the very equation of Poiseuille for the flow of a true fluid which has been quoted as forming the basis of his measurements, was empirically based on the observation that rate of shear varied directly with the fourth power of the radius and inversely as the length of the tube of flow. The "mathematical" derivation of the variation of velocity gradient with the radius of the tube, etc., followed as a consequence.

Cotton said that one of the important points which emerged from Blow's paper was that apparently during the period of mastication the rubber molecule underwent no change whatsoever, and that what happened was merely that the structure of the rubber was broken down. If that be the case, he could not quite understand why over-masticated rubber should give such poor results when it was vulcanized, and he asked Blow whether there was a definite period of mastication beyond which one could continue masticating for hour after hour without producing any detrimental effect upon the rubber. Did he consider that the structure of the rubber substance in the raw state persisted during cure, and that if that structure were broken up the effect on the cured sample was definitely detrimental?

Commenting upon Mr. Blow's remarks concerning the effect of carbon black in the rebuilding of the structure, it was asked whether he could suggest from what source energy was derived—for energy must be absorbed from somewhere in the building up of the structure.

Blow, replying to Drakeley, said that the viscosity had been determined in his experiments by the capillary method only. He would have liked to have used a Couette-Hatschek viscometer, but he had not one available. With reference to the apparent contradiction pointed out by Drakeley, he said that the original structure was not built up, but a fresh one due to adsorption of the surface of the carbon black particles. He (Blow) failed to see why this structure should persist in the rubber when it was separated from the carbon black.

With reference to de Waele's remarks, as Stamberger had mentioned, he had done his best to present his paper simply, without discussing the many equations which had been put forward to explain the values obtained. He was fully aware that Herschel had found structure viscosity in rubber sols when pigments were absent. Herschel, however, had used unmasticated rubber whereas over-masticated rubber had been used in this investigation for the very reason that it failed to show any irregularities. It may be noted that it is mentioned in the paper that a variable pressure viscometer was used for a number of the determinations. In spite of the

suggestion of de Waele's that Poiseuille's formula is also empirical, he observed that it held for almost all liquids, whereas in the formulae suggested by Herschel and de Waele factors had been introduced whose physical interpretation was doubtful, and which varied from substance to substance.

Replying to Cotton's query as to why over-masticated rubber produced such poor results on vulcanization, he said one could only say that the vulcanization was the building up of a still stronger structure; if one had a small structure to begin with it all helped, and one could only say that there should be as little mastication as possible. With regard to the source of energy used in building up the structure, he said that when one had reversible gelation, *i. e.*, when the liquid would revert to jelly on standing, heat was evolved during gelation.

[From Transactions of the Institution of the Rubber Industry, Volume 5, No. 6, pages 403 , April, 1930.]

Alternating Behavior of Fatty Acids in Rubber Compounds

T. L. Garner

It has been shown (Bayer, *Ber.*, **10,** 1286 (1877); Garner and Randall, *J. Chem. Soc.*, **125,** 881 (1924)) that the alternations in the melting points and heats of crystallization of normal fatty acids were due to differences in the crystalline structure. Two distinct curves of behavior corresponding to the acids with odd and even numbers of carbon atoms have been shown for the heats of crystallization. McKee (*Naturwissenschaften*, **11,** 938 (1923)) discussing the fats used in the diet of diabetics, states that in the case of glycerides of acids with an uneven number of carbon atoms these are tolerated and their use leads to gradual reduction in acidosis. Glycerides having an even number of carbon atoms break down during metabolism to form butyric, oxybutyric, and acetoacetic acids.

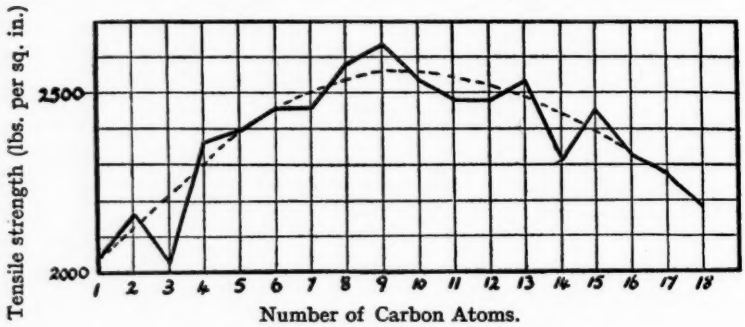

Figure 1—Rubber with Acetone Extract 4.35%

Smith and Boone (*Ind. Eng. Chem.*, **19,** 398 (1927)) have experimented with the addition of purified fatty acids to standard mixings of different kinds of raw rubber. They employed molar proportions of the acid to conform with the recommendations of Kratz, Flower, and Coolidge (*Ind. Eng. Chem.*, **12,** 317 (1920)) that comparisons of organic accelerators should be made with molecularly equivalent amounts of the substances in question. They determined the tensile strength and elongation of the vulcanized products and found no relations between the elongation and the number of carbon atoms present in the acids, but in the case of the tensile strength an alternating effect was evident, the extent of the differences being affected by cure. The tests were carried out on two kinds of rubber, namely, blanket crepe and pale crepe, and the alternating effect of the acids on the tensile strength was more marked in the former case. As pointed out in the paper, the difference in behavior of the two kinds of rubber when treated with fatty acids was presumably due to the difference in the kind and proportions of acids which they originally contained. In fact, in the case of pale crepe the fatty acids already present in the raw rubber masked the alternating behavior to a marked extent, and the curve obtained was in most respects quite different from that obtained with blanket crepe.

Experimental.—In view of the differences observed in the above paper it was thought of interest to determine the effect of the contained fatty acid on the alter-

nating effect of added acids. For this purpose a pale crepe rubber of high acetone extract 4.35 per cent., and one of low acetone extract, 1.82 per cent. were examined, together with pale crepe rubber which had been extracted with acetone for 24 hours. Where necessary the acids used were purified until satisfactory agreement with accepted standards was obtained. A sufficient quantity of each type of rubber was obtained and blended before beginning the experiments, but in the case of the extracted rubber the blending was carried out before extraction, small quantities of the rubber being extracted from time to time and then mixed immediately after drying. The mix used was that adopted by Smith and Boone (*loc. cit.*), 100 parts of rubber, 10 parts of sulfur and 5 parts of zinc oxide. The recommendations of Kratz, Flower, and Coolidge (*loc. cit.*) regarding the comparisons of organic accelerators by using molecular quantities, was followed for the fatty acids, $^1/_{15}$th of a mol being used with each 1000 g. of rubber, as adopted by Smith and Boone. The base mixes were compounded as a master batch and the fatty acid carefully added afterwards.

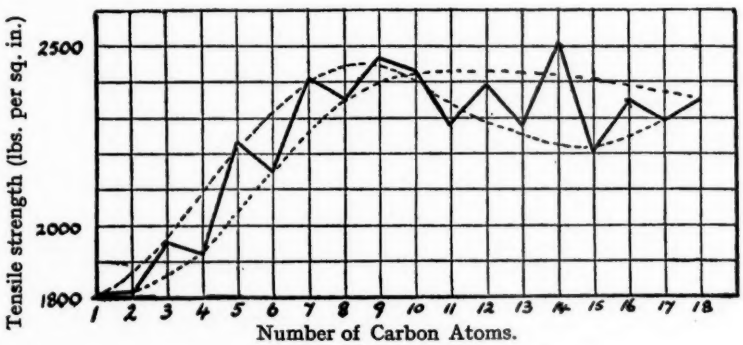

Figure 2—Rubber with Acetone Extract 1.82%

Curing was carried out in 3 in. by 3 in. by $^1/_2$ in. molds, for 80 minutes at 300° F. in each case, and the tensile strengths were determined in a Scott Testing Machine with dumb-bell pieces cut from the blocks. The rubber was rested 24 hours before test and the mean result of four readings agreeing within 100 lbs. was taken as correct.

The results obtained are shown in Figs. 1, 2, and 3. It will be observed that with pale crepe rubber of acetone extract 4.35 per cent., the results show little or no alternating effect; with rubber of acetone value only 1.83 per cent., however, the results show some alternation, but the alternation with the extracted rubber is much more marked and resembles the results obtained by Smith and Boone (*loc. cit.*) with blanket crepe. It is apparent that the results obtained depend entirely on the nature and quantity of acid already present in the rubber and that it is possible to mask completely the effect of added acids by using a rubber containing a high percentage of fatty acids. The 4.35 per cent. extract obtained in one case took 2.8 mg. of potassium hydroxide for saponification and the 1.82 per cent. extract only 1.03 mg. of potassium hydroxide.

It is probable that some variation would be observed by testing at different states of cure as noted by Smith and Boone (*loc. cit.*), and also that a larger proportion of fatty acid than $^1/_{15}$ mol, would show up the alternation better in the case of rubber containing high proportion of fatty acid.

Experiments were also made on the effect of fatty acids on the viscosity of rubber

solution. A 10 per cent. solution of extracted pale crepe rubber in carbon disulfide was first prepared, and also a solution of $^1/_{200}$th mol of each fatty acid in 50 cc. of carbon disulfide. Each acid solution was then mixed with 50 cc. of the 10 per cent. rubber solution, thus giving a 5 per cent. solution and the viscosities were determined using an Ordinary Ostwald Viscometer in a bath at 20° C. All the acids gave a reduction in viscosity but it was not possible to trace any alternating effect in the results.

The effect of molecular quantities of fatty acids on the ash content of rubber mixings was found to show no alternation. A paper dealing with this topic will appear later.

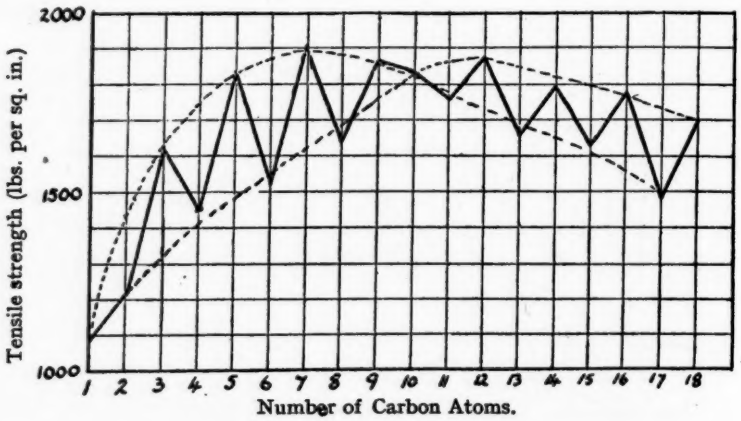

Figure 3—Extracted Rubber

Summary.—Experiments have been carried out which show the alternating effect of fatty acids on the tensile strength of rubber compounds containing them, particularly if the free fatty acid in the raw rubber has been removed. It is shown how the latter variable affects the results obtained, and it is possible with raw rubber of high acid content to mask the alternations completely.

No alternating effect was found on the viscosity of raw rubber solutions, or on the ash value of compounded rubber.

[From India Rubber Journal, Vol. 79, No. 22, page 774, May 31, 1930.]

Influence of Light on the Color of White Rubber

W. J. S. Naunton

Defries and the writer published a note on the effect of sunlight on the color of cured and uncured mixings (*Trans. Inst. Rubber Industry*, **4**, 248 (1928)) in which they ascribed the darkening produced by preliminary exposure to light as being due to a surface over-cure.

Some time later Rimpel and Herrmann published a criticism (*Gummi-Zeitung* **43**, 2270 (1929); see also (*India Rubber J.*, **78**, 943 (1929)) of this work, and contended that the discoloration of a rubber mix on curing after exposure to sunlight was a reduction phenomenon, and independent of state of cure.

Rimpel and Herrmann made the following experiment: Four mixes were prepared, each consisting of rubber, lithopone, and zinc oxide. To the first of these sulfur only, to the second an accelerator, and to the third sulfur and accelerator were added; the fourth received no addition. After exposure to sunlight all the mixings were cured. It was found that the first and fourth mixings were unaffected, but the second and third mixings were discolored to the same extent. The inference was that the discoloration was due to the accelerator as such which behaved like the other reducing agents described in Rimpel and Herrmann's paper.

The writer has since repeated these experiments with the difference that the source of ultra-violet light was a mercury lamp instead of sunlight. The results do not agree with those obtained by Rimpel and Herrmann. The accelerator employed was mercaptobenzothiazole. The first and third samples darkened, whereas the second and fourth samples were almost unchanged. It follows, therefore, that the darkening agent is the sulfur and not the accelerator, in other words, the effect is due to vulcanization. Further proof of this conclusion is shown by the fact that when a pattern is printed by means of a mask on the rubber and given a short cure, the difference in degree of vulcanization between the light and dark parts is shown by wiping over the surface with a rag soaked in naphtha, when the light parts swell so much more than the dark parts that the pattern stands out in relief, in fact so much so as to enable the pattern to be used as a printing block.

Many unsuccessful attempts were made to develop the dark pattern before curing by the use of photographic developers and powerful reducing agents, such as alkaline paraminophenol as described by Rimpel and Herrmann.

It should, of course, be kept in mind that darkening under the action of ultra-violet light can be obtained in a rubber mix in the absence of sulfur and presence of accelerator when the accelerator is of the aldehyde-aromatic amine type, due to the action (probably oxidation) of the light upon the accelerator, and is in no way connected with the presence of the rubber since the accelerator alone will darken under the same conditions. This effect is, of course, in no way connected with the effect described in the original paper by Defries and the writer of this note.

[From India Rubber Journal, Vol. 79, No. 10, page 353, March 10, 1930.]

The Measurement of the p_H Value of Rubber Latex

J. G. Mackay

E. A. Hauser has stated in his Gow Lectures on "The Colloid Chemistry of Rubber" that the most satisfactory method of determining the p_H value of latex is by means of the Wulff p_H tester. This instrument, which is manufactured by Messrs. F. and M. Lautenschlager, Münich 2, S.W. 6, determines p_H value by a colorimetric method. Strips of gelatin which have been impregnated with various indicators to render them suitable for different portions of the p_H range are supplied; the range of p_H values has thus been subdivided into five zones, and a scale of comparison colors is supplied for each of these zones. The principle of the instrument is that gelatin is permeable only to the serum of a turbid dispersion such as latex; when an impregnated strip, or, as it is usually termed, an indicator foil, is dipped into the turbid liquid some serum liquid passes within and produces a change in the color of the indicator; at the same time the gelatin, by swelling, prevents any considerable diffusion of this colored portion of the serum into the bulk of the turbid dispersion. The foil is left in the turbid liquid for one minute and then dried in blotting paper. Its color is then compared with the series of colors on the comparison scale supplied.

An instrument of this type was obtained and experiments were undertaken to determine its accuracy and usefulness.

A series of solutions of p_H values from 4.0 to 12.0 and differing successively by 0.2 p_H were prepared as standards. The solutions of p_H value from 4.0 –10.0 were made up according to the prescriptions of Clark and Lubs (Clark, "The Determination of Hydrogen Ions," pp. 99–107), while those of p_H value from 10.0–12.0 were prepared from the British Drug Houses Universal Buffer Solution as described by Prideaux and Ward (*J. Chem. Soc.*, **1924**, 125, 426).

It was then necessary to check the accuracy of making up these standard solutions. In the first place 10-cc. samples of each solution were colored with 0.5-cc. portions of 0.04 per cent. solutions of suitable indicators in clean dry test tubes. The indicators used and their most appropriate range of p_H are:

Bromophenol blue.....	4.0– 4.4
Bromocresol green.....	4.4– 5.2
Chlorophenol red.....	5.2– 6.2
Bromocresol purple.....	6.0– 6.6
Bromothymol blue.....	6.4– 7.2
Phenol red.....	6.8– 7.6
Cresol red.....	7.4– 8.0
m-Cresol purple.....	7.8– 8.8
Thymol blue.....	8.8– 9.6
Thymol phthalein.....	9.4–10.4
Alizarin yellow.....	10.2–11.4
Tropæolin O.....	11.2–12.0

At no point in the range of p_H values represented by these colored samples was there an unusually great change in shade, and we can therefore conclude that the graduation in p_H value is regular throughout. The p_H values of several solutions throughout the series were then determined by the electrometric method, using a point platinum electrode; each was accurate to within 0.1 p_H. It was therefore

concluded that the standard solutions had been prepared with an accuracy sufficient for our purpose.

The p_H values of these standard solutions were then estimated by means of the appropriate indicator foils and comparison scales of the Wulff p_H tester.

Range I (p_H *2.6–5.0*).—Only the region from p_H 4.0–p_H 5.0 could be studied and within these limits the instrument is accurate in the region of p_H 4.0–4.4. It would be very difficult to distinguish between p_H values from 4.6–5.0 because the foils show gradations in shades of blue and display none of the tendency toward purple which is noticeable in the colors on the comparison scale.

Range II (p_H *5.0–7.2*).—In this range the instrument will give accurate results in the region from p_H 5.8–7.2, but is inaccurate in the region of p_H from 5.0–5.6, because the shades of yellowish green which are displayed against these p_H values are not sufficiently differentiated.

Range III (p_H *7.0–9.0*).—Here the instrument is accurate only from p_H 8.0–9.0. With all the standard solutions of p_H values from 7.0–7.8 the foils gave the same yellow color; the steady gradations given on the scale were not obtained in practice. Probably this portion of the range is without the "virage" of the indicator.

Range IV (p_H *8.2–10.8*).—Accurate results are obtained from p_H 8.6–p_H 10.8. Differentiation between the colors for p_H 8.2 and p_H 8.4 is very difficult indeed.

Range V (p_H *10.1–12.6*).—Only the region from 10.1–12.0 could be studied. Within this region accurate results can be obtained between p_H values of 10.6 and 12.0. From 10.1–10.6 it is difficult to distinguish the shades of color. It must be noticed in using this range that no time should be wasted between removing the foil from the solution of unknown p_H and comparing with the standard, because absorption of CO_2 is fairly rapid owing to the considerable surface exposed. With care and rapidity, however, accurate results can be obtained.

Preserved latex is always alkaline; at a p_H of about 6.0 latex will coagulate. The instrument will, therefore, be of considerable use in work with latex, since the following are the regions in which the various ranges are sufficiently accurate to be useful.

	p_H
Range II	5.8– 7.2
Range III	8.0– 9.0
Range IV	8.6–10.8
Range V	10.6–12.0

The only disadvantage is the break in continuity between 7.2 and 8.0, and this can be surmounted by using the instrument in conjuncton with a series of standard solutions of known p_H.

The author desires to thank his employers, the North British Rubber Co., Ltd., for permission to publish this article.

[From India Rubber Journal, Vol. 79, No. 7, pages 239–243, February 15, 1930.]

Experiments on the Causes of the Deterioration of Ebonite when Exposed to Light and Air

D. M. Webster and B. D. Porritt

In a previous publication (*India Rubber J.*, **78**, 307 (1929)), giving the results of some preliminary experiments having as object the elucidation and, if possible, the elimination of the causes responsible for the marked electrical deterioration shown by ebonite on exposure to light, it was shown that hydrogen sulfide is evolved in appreciable amounts (*a*) when ebonite is exposed to sunlight, and (*b*) when the material is moderately heated. Quantitative results, moreover, were given showing the amounts of this gas evolved by a sample of pure rubber-sulfur ebonite in equal times at various temperatures ranging from 100° C. to 180° C.

At this stage further work was evidently necessary with a view to correlating the evolution of hydrogen sulfide with the formation of the highly conducting surface layer responsible for the deterioration in electrical properties shown by ebonite on exposure, and to ascertaining the source from which the hydrogen sulfide was derived. The present experiments deal with this second part of the work, and carry the investigation a step further.

I. Nature of the Conducting Film

With the object of investigating more closely the conducting surface film, the following experiment was carried out. A thin strip of 65 : 35 rubber-sulfur ebonite was prepared and subjected to a prolonged extraction with acetone in a Soxhlet apparatus in order to remove free sulfur. It was then placed in a glass tube, containing a small quantity of distilled water, which was separated from the ebonite by a slight constriction in the tube wall. The opening of the tube was sealed with a cork through which passed one end of a U-tube containing soda-lime, thereby permitting the entrance of air while excluding any gas of an acid nature. The apparatus was then exposed on the roof of the laboratory during the whole of August.

At the end of the four weeks the ebonite strip was removed from the tube and the surface washed carefully with a small quantity of distilled water, which, together with the water in the bottom of the tube, was carefully tested. The water was found to be acid and distinct traces of sulfurous and sulfuric acids were detected.

The conductivity of the surface film of a piece of ordinary ebonite after exposure is evidently due, therefore, to the presence of traces of the above electrolytes, and these, it would appear, are produced not merely by the oxidation of the free sulfur, but also by the oxidation of hydrogen sulfide, which is evolved continuously, though at an extremely slow rate at the ordinary temperature, from the ebonite.

II. Source of the Hydrogen Sulfide and the Reaction Involved in Its Production

Attention was directed next to the source from which the hydrogen sulfide was derived and to the reaction or reactions involved in its production. As already mentioned, some preliminary experiments had been made in which it was found that ebonite evolved hydrogen sulfide when heated, and that the amount evolved

in a given time increased rapidly with increasing temperature. It was decided to investigate this question more fully, and in particular to study the rates of evolution of the hydrogen sulfide at different temperatures for one or more samples of ebonite.

(*1*) *Method.*—The method adopted consisted in measuring the amounts of hydrogen sulfide evolved during measured intervals of time from a weighed quantity of ebonite dust which was heated at a constant temperature in an atmosphere of hydrogen. The arrangement used was the following:

A steady stream of hydrogen was passed over a weighed quantity of the dry extracted dust (approximately 3 grams) contained in a U-tube which was immersed in an oil bath filled with hydrogenated cottonseed oil. To prevent any dust from being carried away by the gas stream, a plug of asbestos (previously ignited) was inserted in the exit limb of the U-tube. The hydrogen, which was generated from zinc and hydrochloric acid, was purified by being passed in succession through a soda-lime tube, a solution of potassium permanganate, a phosphorus pentoxide tube, a silica tube heated to bright redness, and finally a second phosphorus pentoxide tube. A mechanical stirrer, in conjunction with a small mercury thermoregulator, kept the temperature of the oil bath approximately constant ($\pm 1°$ C.). Two Drechsel wash-bottles containing silver nitrate solution (approximately $N/10$) were used to absorb the hydrogen sulfide, and by means of a three-way tap it was possible to switch over to fresh bottles without the loss of more than the merest trace of the gas. In certain of the experiments, to be referred to later, the silver nitrate was replaced by an ammoniacal solution of hydrogen peroxide with the object of checking the accuracy of the hydrogen sulfide determinations by the use of two entirely different methods of estimation.

In carrying out an experiment the procedure adopted was as follows: The U-tube containing the ebonite was connected to the gas supply and absorption bottles, being meanwhile suspended by a clamp alongside the bath, and hydrogen was passed through until the whole of the air had been expelled. The tube was then immersed in a smaller oil bath heated to 100° C. (at which temperature there is no appreciable evolution of hydrogen sulfide) and after a few minutes transferred to the larger bath. By allowing the temperature of this bath to rise a degree or two above the working temperature before introducing the U-tube, the slight cooling effect due to the latter was compensated for, and the working temperature attained almost immediately.

The absorption bottles were changed at increasing time intervals, as the evolution was found to be rapid at first and then to fall off. The silver sulfide precipitated during each interval was collected, washed free from silver nitrate, reduced to silver by ignition in an atmosphere of hydrogen, and the amount of hydrogen sulfide calculated from the weight of silver. In the alternative method of absorption the hydrogen sulfide was oxidized to ammonium sulfate by means of the ammoniacal hydrogen peroxide and estimated by precipitation of the sulfate as barium sulfate.

At the conclusion of each experiment the total loss in weight of the U-tube was determined, the tube being weighed under the same conditions as at the beginning of the experiment. It was found that in addition to the hydrogen sulfide evolved, a very small amount of volatile organic matter was given off, part of which condensed round the upper part of the exit limb of the U-tube. After the tube had been weighed this was removed and the tube again weighed in order to determine the actual loss in weight of the dust. Lastly, the residue in the tube was examined for:

(1) Total sulfur.

(2) Extractable material. (Samples were extracted for 24 hours with carbon disulfide, followed by a further 24 hours with acetone.)

(3) Extractable sulfur.

(4) Fixed sulfur (*i. e.*, total *minus* extractable).

(*2*) *Material Used.*—Samples of pure rubber-sulfur ebonite from three different sources were used in the experiments to be described. These gave the following figures on analysis:

TABLE I

	No. 1	No. 2	No. 3
Ash	0.38%	0.20%	0.53%
Total sulfur	33.25	33.77	33.92
Organic matter (by difference)	66.37	66.03	65.55
Free sulfur	3.19	2.70	4.34
Combined sulfur	29.55	31.06	29.48
Acetone extract	6.12	4.61	6.81

In each case a quantity of fine dust was prepared from the sample by filing, and extracted for 48 hours with acetone in Schidrowitz extractors. Precautions were taken against incomplete extraction due to channelling, the treatment being interrupted from time to time and the dust thoroughly mixed. After extraction the bulk of the acetone was removed by means of filter paper, and the dust finally dried at 70° C. to constant weight in a current of hydrogen. The extracted material so prepared was kept in the dark in tightly stoppered bottles.

(*3*) *Experimental Results.*—The various experiments carried out, together with the results obtained, will be found in the tables and in Figs. 1 and 2. Table II and III illustrate typical experiments, while Table IV gives a summary of all the work done.

TABLE II

EXPERIMENT No. 3 — TEMPERATURE 200° C. — No. 1 EBONITE

Weight of Ebonite Taken, G.	Time in Hours	Weight of Silver Obtained, G.	Total Weight of Silver, G.	Total Weight of H_2S, G.	H_2S in G. per Gram of Ebonite
	0–1	1.0896	1.0896	0.1716	0.0665
	1–3	0.2907	1.3803	0.2172	0.0842
	3–5	0.0937	1.4740	0.2320	0.0899
	5–10	0.1002	1.5742	0.2477	0.0960
2.5799	10–24	0.1211	1.6953	0.2668	0.1034
	24–48	0.0853	1.7806	0.2803	0.1086
	48–74	0.0564	1.8370	0.2891	0.1121
	74–97	0.0435	1.8805	0.2961	0.1148
	97–119	0.0325	1.9130	0.3011	0.1167

Hydrogen sulfide evolved..... = 0.3011 g. = 11.67% of the weight of ebonite
Loss in weight of U-tube..... = 0.3145 g. = 12.2 % of the weight of ebonite
Loss in weight of ebonite (*i. e.*, allowing for the volatile organic matter) = 0.3276 g. = 12.7 % of the weight of ebonite

TABLE III

EXPERIMENT No. 4 — TEMPERATURE 200° C. — No. 1 EBONITE

Weight of Ebonite Taken, G.	Time in Hours	Weight of $BaSO_4$ Obtained, G.	Total Weight of $BaSO_4$, G.	Total Weight of H_2S, G.	H_2S in G. per G. of Ebonite
	0–1	1.2120	1.2120	0.1768	0.0643
	1–3	0.3475	1.5595	0.2276	0.0828
	3–5	0.1161	1.6756	0.2446	0.0890
	5–11	0.1170	1.7926	0.2617	0.0952
2.7502	11–24	0.0996	1.8922	0.2761	0.1004

24–50	0.1091	2.0013	0.2920	0.1062
50–71	0.0400	2.0413	0.2978	0.1083
71–100	0.0488	2.0901	0.3049	0.1109
100–127	*0.1383	2.2284	0.3251	0.1182

Hydrogen sulfide evolved..... = 0.3251 g. = 11.8% of the weight of ebonite
Loss in weight of U-tube..... = 0.3614 g. = 13.1% of the weight of ebonite
Loss in weight of ebonite (*i. e.*, allowing for the volatile organic matter) = 0.3773 g. = 13.7% of the weight of ebonite

* High on account of an accidental rise in temperature during the last few hours of the run.

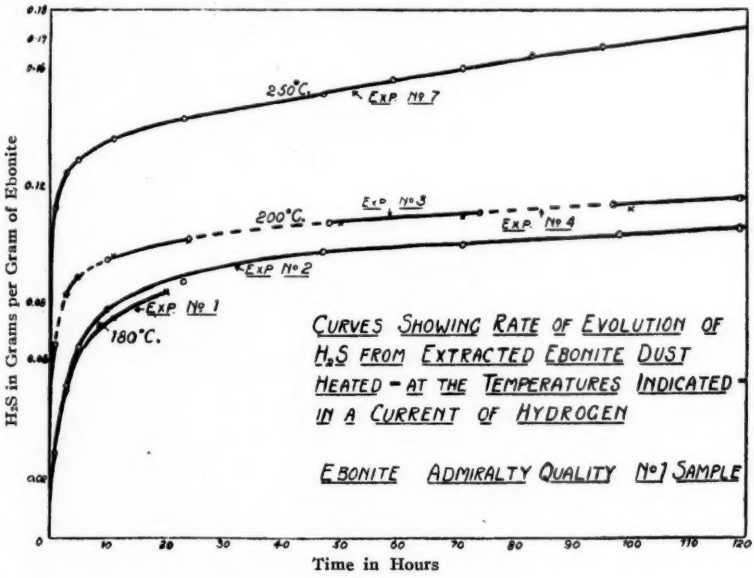
250°C.
Exp. No 7
200°C.
Exp No 3
Exp No 4
Exp No 2
Exp No 1
180°C.
Curves Showing Rate of Evolution of H₂S from Extracted Ebonite Dust Heated - at the Temperatures Indicated in a Current of Hydrogen
Ebonite Admiralty Quality No 1 Sample
H₂S in Grams per Gram of Ebonite
Time in Hours

Figure 1

Of the experiments enumerated, the first was in the nature of a trial. No arrangements had been made for continuous running, and the experiment had therefore to be stopped each night and started the following morning, so that the results obtained were only approximate. It furnished, nevertheless, a certain amount of useful information, and the curve obtained has been included in Fig. 1, since, so far as it goes, it confirms fairly well the results obtained in Experiment No. 2. For this experiment the apparatus was much improved, being substantially that described, and the experiment was allowed to run continuously for 119 hours.

Experiment No. 3 was carried out along exactly the same lines as No. 2, but with the working temperature increased by 20° to 200° C. No. 4 was a repeat at the same temperature with ammoniacal hydrogen peroxide substituted for silver nitrate in the absorption apparatus—as already explained. Further, it was at this stage that the heated silica tube was introduced, since it was thought that the traces of oxygen certain to be present in the hydrogen might be catalyzing the reaction. The two experiments, as will be seen from Tables II and III, and also from Fig. 1, yielded remarkably concordant results showing:

(1) That both methods used for estimating the hydrogen sulfide were accurate.

TABLE IV

No. of Experiment	Description	Duration, Hours	H_2S Evolved as % on Weight of Ebonite	Loss in Weight of U-tube as % on Weight of Ebonite	Loss in Weight of Ebonite, %	Analysis of Residues after Heating: CS_2 + Acetone Extract	Total Sulfur	Sulfur in Extract (All Combined)	Sulfur in Residue, after Extraction
1	No. 1 Ebonite at 180° C. H_2S estimated as Ag_2S	20	8.5	...	..	...	...	..	...
2	No. 1 Ebonite at 180° C. H_2S estimated as Ag_2S	119	10.5	11.7	12.1	10.11 (8.88)	24.02 (21.10)	1.35 (1.19)	22.49 (19.76)
3	No. 1 Ebonite at 200° C. H_2S estimated as Ag_2S	119	11.7	12.2	12.7	10.99 (9.59)	23.58 (20.59)	*2.84 (2.55)	20.74 (18.10)
4	No. 1 Ebonite at 200° C. H_2S estimated as $BaSO_4$	119	11.8	13.1	13.7	10.97 (9.49)	23.54 (20.32)	*2.78 (2.40)	20.76 (17.92)
5	No. 2 Ebonite at 200° C. H_2S estimated as $BaSO_4$	119	11.4	13.6	13.8	12.75 (10.99)	24.06 (20.74)	*2.27 (1.96)	21.79 (18.78)
6	No. 3 Ebonite at 200° C. H_2S estimated as $BaSO_4$	119	11.2	11.3	12.4	10.70 (9.37)	23.53 (20.62)	*2.02 (1.77)	21.51 (18.84)
7	No. 1 Ebonite at 250° C. H_2S estimated as Ag_2S	126.5	18.0	20.90	22.1	...	...	..	...

* By difference.

NOTE: In Columns 7–10 the figures unbracketed are percentages referred to the weight of ebonite after heating, while those in brackets are the same figures expressed as percentages of the weight of ebonite before heating.

(2) That small quantities of oxygen had no appreciable effect on the reaction.

Up to this point the ebonite used had been the No. 1 sample. Experiments 5 and 6 were next carried out, using samples No. 2 and No. 3. As will be seen from Fig. 2, the results were substantially the same as those obtained with the No. 1 quality.

Finally, the working temperature was raised another 50° to 250° C. (Experiment No. 7). At the conclusion of the experiment it was found that the ebonite had partially melted under the treatment, and the residue in the tube was therefore not analyzed as in the previous experiments. For the same reason, no attempt was made to raise the working temperature still further. Here it may be remarked that while in Experiments 1–6 the residues after heating were very similar in general appearance to the original dust, a marked change in color occurred as a result of the treatment. Whereas the dust before heating was a dark brown, the residue in each of the above experiments was distinctly reddish in appearance.

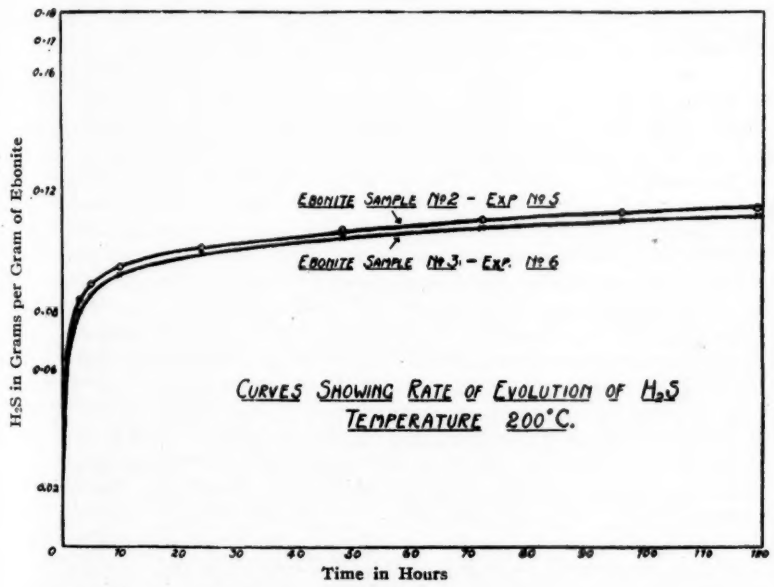

Figure 2

III. Discussion of Results

An early hypothesis formed in the course of the investigation may be mentioned. From the results of the first two experiments on the rate of evolution of hydrogen sulfide it was thought that the latter might possibly be derived from the decomposition of only a portion of the ebonite—more unstable than the rest—and that once this portion had decomposed no more hydrogen sulfide would be given off. The curve obtained in Experiment No. 2, for example, shows a rapid decline in the amount of hydrogen sulfide being evolved after about 20 hours' heating, and the slow rate of evolution during the remainder of the run appeared to indicate an end point when approximately one-third of the sulfur in the original material had been removed as hydrogen sulfide. Such a result would have been highly interesting,

suggesting the possibility of improving ebonite by subjecting it to a preliminary heating in order to break up the unstable portion.

As the results show, however, the above was not borne out by the later experiments. In no case was an end point reached, and the latter portions of all the curves obtained were linear and showed no signs of becoming asymptotic to the time axis. The various curves are, in fact, merely typical of the heterogeneous reaction involved, a type of reaction in which the rate is closely connected with the surface of the reacting material or materials. The steep part of each curve probably corresponds to the decomposition of the surface layer of each particle of the material and the flat portion is presumably determined by the rate of migration of hydrogen sulfide molecules from the interior to the surface. As, however, the study of the dynamics of the reaction was outside the scope of the investigation, this subject was not pursued further.

From Table IV it will be seen that in all the experiments the weight of hydrogen sulfide evolved is in good agreement with the observed loss in weight. Only in Experiment No. 7 is the difference appreciable, and this must be ascribed to the loss by volatilization of a greater proportion of volatile hydrocarbons, due to the higher working temperature. Further, the sulfur contents of the residues after heating as determined by analysis are in good agreement with values which can be calculated from the original sulfur content, the loss in weight, and the weight of hydrogen sulfide evolved. In Experiments Nos. 2 and 3, for example, the calculated figures are 24.82 per cent. and 23.89 per cent., and those actually found 24.02 per cent. and 23.58 per cent., respectively. It is clear, therefore, that all the sulfur which is removed by the heat treatment goes off as hydrogen sulfide, and from the nature of the curves in Figs. 1 and 2 it seems reasonable to suppose that the whole of the sulfur might be removed in the same manner by prolonged heating.

It will be seen that the material after heating, in addition to having a lower sulfur content, is no longer completely insoluble in acetone and carbon disulfide. In the experiments at 200° C. an extract of approximately 11 per cent. was obtained in each case. These extracts consisted of brown resinous bodies containing combined sulphur. No free sulfur was found when the extracts were tested according to the method of Davis and Foucar (*J. Soc. Chem. Ind.*, **31**, 100 (1912)). The residual materials from the heating experiments were also tested for unsaturation by the usual bromine absorption method. In every case they were found to be unsaturated—a result to be expected—and the extracted residue from Experiment No. 4 absorbed approximately 0.4 g. bromine per gram.

IV. Conclusion

From the above it is evident that the reaction which takes place when ebonite is heated in an indifferent gas at temperatures up to 250° C. is the removal of the sulfur by the splitting out of hydrogen sulfide with the formation of unsaturated substances. It has not been found possible to formulate from the data obtained any scheme showing the nature of the decomposition in terms of the empirical chemical composition of ebonite, though it would seem from the results of the examination of the residues that the decomposition takes place by steps.

It has already been mentioned that the evolution of hydrogen sulfide from ebonite takes place at the ordinary temperature, and, further (cf. *India Rubber J.*, **78**, 307 (1929)), that the reaction appears to be catalyzed by light. Under these conditions, which represent those obtaining during what may be termed the "normal aging" of ebonite in use, the reaction may not, of course, be merely that outlined above. Simultaneous oxidation of the material will probably take place, with the formation of products analogous to those found in the case of soft vul-

canized rubber—rubber derivatives containing both sulfur and oxygen. To what extent these oxidation products affect the properties of ebonite as a dielectric is not known, but so far as surface leakage is concerned it seems unlikely that they will play any great part, this being due rather to the surface film of condensed moisture containing dissolved electrolytes. Since, as has been shown, these electrolytes are derived not merely from the small amount of free sulfur left uncombined after the vulcanization process, but also from the decomposition of the basic material, it is obvious that the problem of the electrical deterioration of ebonite is bound up with the chemical stability of the material, and that to eliminate the former it will be necessary to increase the latter.

In conclusion it may be remarked that, while the results of the investigation up to date have not yielded a solution of the problem, they have to some extent cleared the ground. Although it is hoped that a solution will ultimately be found, it would appear that the problem is not one to be solved easily.

V. Summary

(1) The surface film of a sample of ebonite—containing no "free" sulfur—has been shown to develop distinct traces of sulfurous and sulfuric acid after exposure to light in a moist atmosphere for a period of four weeks.

(2) The above acids appear to result from the oxidation of hydrogen sulfide formed through the decomposition of the hydrocarbon-sulfur nucleus of the ebonite.

(3) The rate of evolution of hydrogen sulfide from ebonite when heated in an atmosphere of hydrogen has been investigated for temperatures ranging from 180° to 250° C., and for three different samples of ebonite.

(4) For a given temperature the rate of evolution is rapid at first, but falls off quickly and finally remains uniform over a long period, the latter portion of the time-H_2S curve being linear within the limits of experimental error.

(5) The rate of evolution increases with increasing temperature.

(6) Under the heat treatment the ebonite changes in color, becoming reddish in appearance. At the same time it becomes unsaturated and more and more soluble in acetone and carbon disulfide.

(7) The decomposition which takes place on heating ebonite to temperatures not exceeding 250° C. does not appear to give rise to appreciable amounts of either free sulfur or volatile organic compounds.

(8) The bearing of the above results on the problem of the electrical deterioration of ebonite has been discussed.

The authors thank the Board of Management of the Research Association of British Rubber Manufacturers for permission to publish these results, which formed the Association's Research Report No. 18.

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3-Methyl-1,3-Pentadiene[1]

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A new set of reactions is given for preparing 3-methyl-1,3-pentadiene. Ethyl methyl ketone and acetaldehyde are aldoled to form 3-methyl-4-hydroxy-2-pentanone, and this keto alcohol is then catalytically hydrogenated to the corresponding glycol, which on being dehydrated forms the 1,3-diene. No 1,2-diene can form during the dehydration. Attempts to polymerize the 1,3-diene to rubber-like products were only partially successful. The additional evidence given shows that the polymerization of 1,3-dienes to rubber-like products does not depend solely on the presence of a vinyl group.

HARRIES, in his book, "Investigations on Natural and Artificial Varieties of Rubber" (*4*), wrote that further systematic work on the innumerable homologs and analogs of butadiene would doubtless produce substances which could easily be polymerized to rubber-like products. He himself had worked chiefly only on 1,3-butadiene or erythrene, β-methylbutadiene or isoprene, α-methylbutadiene or piperylene, and β,γ-dimethylbutadiene. The patent literature, he says, cites many others that could be polymerized to rubber under the usual conditions, but he adds that the possibilities may be quite limited, because, for example, he has found that α,α-dimethylbutadiene (2-methyl-2,4-pentadiene),

$$\begin{matrix} CH_3 \\ \diagdown \\ \quad C{:}CH.CH{:}CH_2 \\ \diagup \\ CH_3 \end{matrix}$$

"presents difficulties in polymerization to a rubber," and

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similarly with α-phenylbutadiene (1-phenyl-1,3-butadiene), $C_6H_5.CH:CH.CH:CH_2$.

Macallum and Whitby (*10*) also discuss this subject, stating: "It would appear that methyl substitution in the terminal positions of butadiene has, compared with such substitution in the middle positions, an unfavorable effect on the ease of polymerization," and "that increase in the number of methyl substituents in butadiene diminishes the ease of polymerization." They prepared a new derivative—namely, α,β,γ,δ-tetramethylbutadiene (3,4-dimethyl-2,4-hexadiene)—and showed that it has "little or no tendency to undergo thermopolymerization" to a rubber.

The writers undertook to prepare a simple homolog of butadiene which could easily be obtained pure and in good yield, and then to test its polymerization possibilities, especially to a rubber-like product. It was decided to form the double bonds in the final compound by a dehydration process and therefore to prepare a glycol in the previous step. The following consideration also seemed important. 1,3-Butadiene, isoprene, and piperylene, on being polymerized, give synthetic rubbers which have better practical properties than those obtained from 2,3-dimethyl-1,3-butadiene (*6*). In view of the structural relationships of these hydrocarbons

$CH_2:CH.CH:CH_2$	$CH_2:\dot{C}.CH:CH_2$	$CH_3.CH:CH.CH:CH_3$	$CH_2:\dot{C}.\dot{C}:CH_2$
	CH_3		$H_3C\ CH_3$
Butadiene	Isoprene	Piperylene	2,3-Dimethyl-1,3-butadiene

it was thought that the vinyl grouping, $\cdot CH:CH_2$, present in the first three, might be responsible for this difference in the rubber polymers, and therefore that the diene should contain such a grouping. The hydrocarbon chosen was 3-methyl-1,3-pentadiene. It had already been prepared by Abelmann (*1*), who used the following reactions:

$$CH_3.CH:\dot{C}.CHO \xrightarrow{CH_3MgI\text{ and hydrolysis}} CH_3.CH:\dot{C}.CH(OH).CH_3 \xrightarrow{\text{Concd. HCl}}$$

Tiglic aldehyde — 3-Methyl-4-hydroxy-2-pentene

$$CH_3.CH:\dot{C}.CHCl.CH_3 \xrightarrow{\text{Quinoline, at 180° C.}} CH_3.CH:\dot{C}.CH:CH_2$$

3-Methyl-4-chloro-2-pentene — 3-Methyl-1,3-pentadiene

The position of one double bond is fixed by the starting product, and the position of the other one can only be as shown, provided no rearrangements have taken place. Abelmann apparently did not try to polymerize it.

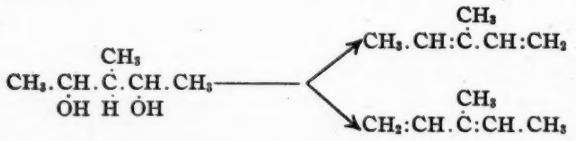
The writers' method consists in aldoling ethyl methyl ketone and acetaldehyde to form the keto alcohol, 3-methyl-4-hydroxy-2-pentanone,

$$CH_3.CO.\dot{C}H.CH(OH).CH_3$$

reducing this catalytically to the corresponding glycol, 3-methyl-2,4-pentanediol,

$$CH_3.CH(OH).CH.CH(OH).CH_3$$

and dehydrating this glycol. Usually in dehydration processes the hydroxyl group is eliminated with a hydrogen atom from an adjacent secondary or tertiary carbon in preference to one from a primary carbon. On this account it no doubt often happens that a 1,2-diene is formed instead of the desired 1,3-diene, or the 1,2-diene forming at the same time constitutes an impurity which is very difficult to remove and also cuts down the yield. However, since the above glycol is symmetrical, and since it is most likely that one of the hydroxyl groups would be eliminated along with the hydrogen on the tertiary carbon "first," it follows that the second hydroxyl must be eliminated with a hydrogen from an end (primary) carbon, and give the same 1,3-diene in either case:



A 1,2-diene cannot be formed. There is, however, the possibility of each hydroxyl group being eliminated with a hydrogen from an adjacent end (primary) carbon, forming a 1,4-diene. This compound probably does form but only to a limited extent.

The keto alcohol, the glycol, and the hydrocarbon had already been prepared by others, but the methods described herein are different.

Polymerization

There are three well-known methods of polymerizing butadiene and its simple homologs to rubber-like products (*5*, *12*)—namely, (*a*) heating alone or in acetic acid solution, in a sealed tube for a certain time at 60–100° C. (the tube generally contains some air); (*b*) heating or allowing to stand in the presence of metallic sodium in an atmosphere of air or carbon dioxide; and (*c*) heating in the presence of peroxides, especially benzoyl peroxide. The first and third methods are probably the same fundamentally. The 3-methyl-1,3-pentadiene was treated according to these three general methods. Soft, tacky, rubbery products were obtained by long heating in air and in the presence of benzoyl peroxide, while oily, sticky polymers were obtained by heating, or by long standing, with sodium. The yields varied from 16 to 52 per cent of the total weight.

Experimental

3-Methyl-4-Hydroxy-2-Pentanone—This was prepared according to the general method of Kyriakides (*8*, *11*), by the action of a dilute solution (10 per cent) of potassium hy-

droxide on an equimolecular mixture of acetaldehyde and ethyl methyl ketone in ether solution. The amount of alkali was 0.2 per cent of the weight of the aldehyde-ketone mixture and the temperature of the vigorously stirred reaction mixture ranged from 20° to 40° C. The residual alkali was neutralized with tartaric acid, and the mixture was filtered from the insoluble potassium tartrate, dried, and distilled. The boiling point was 66–8° C. at 1 mm.; Salkind (*11*) gives 74–5° C. at 10 mm. The actual yields were only 10 to 12 per cent of the theory, but in each case large amounts of unreacted materials were recovered.

3-Methyl-2,4-Pentanediol—This keto alcohol was reduced by hydrogenation according to the method of Adams (*2, 3, 7, 13*). The catalyst was prepared by fusing 4.5 grams of chloroplatinic acid and 45 grams of sodium nitrate at 500° C. A trace of ferrous sulfate was added as a promoter. The catalyst was added directly to the keto alcohol (146 grams) and no solvent was used. The hydrogenation was carried out at room temperature during 28 hours, and it was found that the rate of absorption of hydrogen was greatest within the first hour. The fraction boiling 82–90° C. at 1 mm. was taken as the glycol. Salkind (*11*), who used sodium amalgam for the reducing agent, gives for the boiling point 103–5° C. at 10 mm. The yield was 63 per cent.

3-Methyl-1,3-Pentadiene—Ninety-two grams of the 3-methyl-2,4-pentanediol were dehydrated by distilling under a Hempel column in the presence of 2 grams of aniline hydrobromide and 2 cc. of concentrated (48 per cent) hydrobromic acid (*9*). The temperature of the outgoing vapors was kept below 90° C. The distillate separated into two layers, the oil layer weighing 60 grams and the water layer, 22 grams. Complete decomposition should have given 28 grams of water, not counting that contained in the hydrobromic acid. Nothing was collected in the acetone–solid carbon dioxide trap attached to the system. The oil layer was separated, dried, and distilled. The fraction boiling above 85° C. was treated again with hydrobromic acid but practically no more low boiling material was obtained. The fraction boiling under 85° C. was redistilled twice over metallic sodium, giving 27 grams of a hydrocarbon boiling at 77–78° C.; refractive index (Abbé refractometer), $n_D^{21} = 1.4561$. Abelmann (*1*) gives a boiling point of 76–9° C., and $n_D^{16.5} = 1.45427$. The yield was 42 per cent of the theory.

Polymerization—Samples of the above diene were sealed up (*a*) with air, and (*b*) with metallic sodium, and allowed to stand for 1 month at room temperature, but no change in volume or in viscosity was noticed after this period of time. After 29 months, however, the sample with sodium had become very viscous and light brown in color, whereas the one in air showed no change. The sample with sodium was treated with alcohol, and a very viscous, sticky, somewhat rubbery product obtained. The yield was 52 per cent.

Sample (*a*) was opened, sodium wire added, re-sealed, and heated for 24 hours at 72° C. Since there was no apparent change except in the colour, which had become brownish, it was heated for 24 hours more at 102° C. It became very viscous, and the viscosity increased somewhat after a further heating for 24 hours at the same temperature. Treatment with alcohol gave 41 per cent of a very viscous, sticky polymer.

Other samples were sealed up (*c*) with air, and (*d*) with about 5 per cent of benzoyl peroxide, and heated for 1 month at 100° C. In these two tubes there was a slight increase in viscosity and a slight decrease in volume, greater in (*d*) than in (*c*). After further standing for 29 months at room temperature these changes had become even greater. The volume in each case decreased approximately 10 per cent. The clear, colorless solutions were precipitated with alcohol. Sample (*c*) gave a clear, colorless, soft, tacky, rubbery polymer (16 per cent), and (*d*) gave 29 per cent by weight of a similar product. All the products slowly oxidized to resin-like substances in the air.

Note—When this article was written for publication it was thought that all the polymerization tubes had been destroyed. However, shortly after the presentation of the paper at the Atlanta meeting they were found and further examined as recorded above.

Conclusions

3-Methyl-1,3-pentadiene can be prepared pure without difficulty. However, unlike butadiene, isoprene, piperylene, and 2,3-dimethyl-1,3-butadiene, it apparently does not polymerize to an elastic, resilient solid product, and therefore the polymerization of 1,3-dienes to rubber-like products does not depend solely on the presence of the vinyl group.

Literature Cited

(1) Abelmann, *Ber.*, **43**, 1583 (1910).
(2) Adams and Shriner, *J. Am. Chem. Soc.*, **45**, 2171 (1923).
(3) Carothers with Adams, *Ibid.*, **45**, 1071 (1923).
(4) Harries, "Untersuchungen über die natürlichen und künstlichen Kautschukarten," p. 250 (1919).
(5) Harries, *Ibid.*, p. 170.
(6) Harries, *Ibid.*, pp. 193, 170, 207, 199; and unpublished work of the authors.
(7) Kaufmann with Adams, *J. Am. Chem. Soc.*, **45**, 3029 (1923).
(8) Kyriakides, *Ibid.*, **36**, 532 (1914).
(9) Kyriakides, *Ibid.*, **36**, 987 (1914).
(10) Macallum and Whitby, *Trans. Roy. Soc. Can.*, III, **22**, 39 (1928); *Rubber Chem. Tech.*, **1**, 341 (1928).
(11) Salkind, *J. Russ. Phys. Chem. Soc.*, **37**, 486 (1905); *Chem. Zentr.*, **76**, (II) 752 (1905), used potassium cyanide as the condensing agent.
(12) Schotz, "Synthetic Rubber," p. 69 (1926).
(13) Voorhees with Adams, *J. Am. Chem. Soc.*, **44**, 1397 (1922).

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Studies in the Vulcanization of Rubber[1]

I—Thermochemistry of Vulcanization of Rubber

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The heat of vulcanization of rubber by sulfur has been carefully determined over the complete range of combination. The formation of hard rubber is a strongly exothermic reaction, while the formation of soft vulcanized rubber is apparently without heat interchange, even in the presence of an accelerator. The vulcanization of rubber with *m*-dinitrobenzene and selenium is also without heat interchange and only soft vulcanized rubber is formed.

Introduction

WHEN a chemical reaction takes place, it is usually accompanied by an absorption or evolution of heat. The amount of the heat interchange is not a direct measure of the chemical affinity involved in the reaction, nor is it a measure of the free energy of the reaction. The heat of reaction, however, is a measure of the total change in internal energy and is of importance, therefore, in calculating the effect of temperature on a reaction and in elucidating the mechanism of it.

Historical

There is comparatively little known about the thermochemistry of vulcanization. In the attempts that have been made to relate vulcanization to a chemical reaction the thermochemical side has been practically neglected. If vulcanization is a chemical reaction, it should follow the laws of mass action and

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the thermal relations should be of importance. Previous work has been of a qualitative nature only.

Weber (*11*) has discussed the heats of formation of the halides of sulfur and attempted to correlate them with their abilities as vulcanizing agents. He also determined the heat of combustion of purified Para rubber and found a value of 10,669 calories per gram. Weber further suggests that vulcanization is an endothermic reaction. The energy change he believed to consist of two parts: first, a large absorption of heat due to the dissociation of S_8 molecules into S_2 molecules; and second, a small evolution of heat when these S_2 molecules were added to the rubber hydrocarbon. The net result was an absorption of heat which he estimated to be about 450 calories per gram of rubber at a combined sulfur of 3.8 per cent.

Seidl (*10*) tried to explain the accelerating effect of litharge thermochemically. He discovered that when a rubber-sulfur-litharge mixture is heated the temperature in the interior of the mass rises above that of the heating bath. He concluded that the evolution of heat thus indicated was due to the reaction of sulfur with the non-rubber constituents of the rubber to form hydrogen sulfide. The hydrogen sulfide in turn reacted with the litharge with a large heat evolution. He did not consider that the reaction of sulfur with rubber might produce any heat interchange.

Williams and Beaver (*12*) heated mixtures of rubber, zinc oxide, sulfur, and various accelerators in a glycerol bath and plotted the temperature of the center of the mass against time. In some cases the internal temperature of the compound rose 62° C. (112° F.) above that of the bath. They concluded from their curves that there is an evolution of heat at the beginning of vulcanization followed by a slight absorption of heat near the end of it. Some of the heat involved was considered to be due to a chemical reaction between sulfur and rubber. They found that the heat effect was increased by an increase in the amount of sulfur present, an increase in temperature, and the presence of accelerators. Attempts were made to calculate values for heats of vulcanization by evaluating the heat conduction through the sample and into the bath. Such a type of calculation is somewhat uncertain, but they found average exothermic values of the heat of vulcanization of 10 calories per gram of compound at 10 per cent sulfur. They worked with not more than 14 per cent sulfur.

Kirchhof and Wagner (*7*) extended the work of Seidl to include magnesium oxide, calcium hydroxide, lead dioxide, lead carbonate, antimony sulfide, and zinc oxide. Kirchhof (*5*) also studied the effect of various accelerators on heat evolution. The presence of natural resins in a litharge stock was shown to enhance the effect.

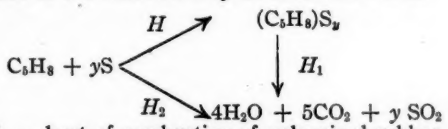
Perks (*9*), using approximately the same method as Williams and Beaver, studied mixtures of rubber and sulfur containing from 0 to 32 per cent sulfur. In some cases he

recorded temperatures in the center of the block of rubber during vulcanization 170° C. (306° F.) above that of the bath. He concluded from his curves that the combination of rubber with sulfur is accompanied by a slight evolution of heat in the first stages of the reaction, followed by an energetic exothermic reaction. Perks was chiefly interested in a method for evaluating the quality of raw rubber.

Bostrom (*1*) has measured directly the heat of vulcanization of rubber with sulfur chloride in benzene solution, using calorimetric methods developed by Hock (*4*) for the measurement of heats of wetting of carbon black and other fillers by rubber. Bostrom found values up to 5.9 calories per gram of rubber for the heat of vulcanization with sulfur chloride.

Method

It is practically impossible to measure directly a heat of reaction at high temperature if the course of the reaction occupies any appreciable time. The law of Hess, which of course is a corollary of the first law of thermodynamics, states that the heat interchange of a reaction is dependent only on the initial and final states of the system and is independent of the course of the reaction. Heats of combustion measurements may thus be used to measure heats of vulcanization. The course of the reaction may be illustrated thus:



where H_1 = heat of combustion of vulcanized rubber
H_2 = heat of combustion of unvulcanized compound
$H = H_2 - H_1$ = heat of vulcanization at temperature at which heats of combustion are determined

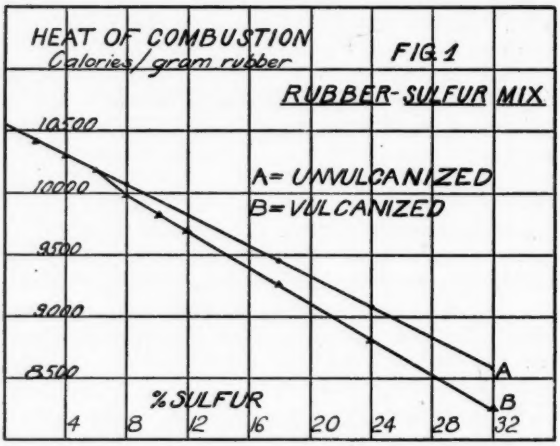
To convert the value of H to the temperature of vulcanization involves calculations based on the specific heats of the reactants and products of the reaction. The values would not be seriously altered by such a transfer from one temperature to the other. It is desirable to find the heat interchange of the reaction

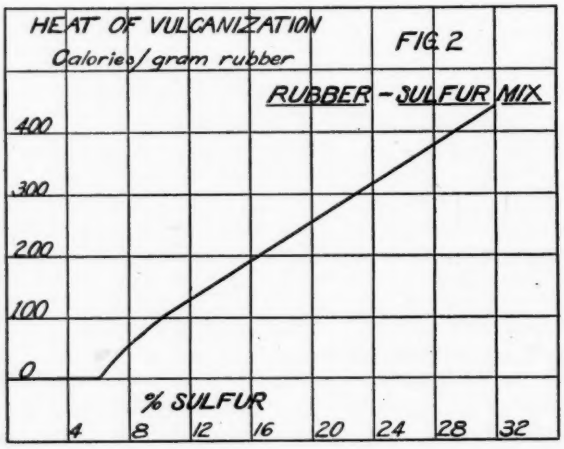
$$C_5H_8 + y\,S = (C_5H_8)S_y$$

as y is varied from zero to unity.

Williams and Beaver (*12*) attempted some preliminary work on the problem, using the same method. They determined the heat of combustion of a mixture of 6.5 per cent sulfur and 93.5 per cent rubber vulcanized to 0.7 and 5.6 per cent combined sulfur. They found no appreciable difference in the values obtained and concluded that there was no measurable heat of vulcanization between the different states of cure. For these compounds they give a heat of combustion of 5825 calories per gram. Kirchhof and Matulke (*6*) give a value for the heat of combustion of rubber of 10,070 calories per

gram. This value is of the correct order of magnitude, whereas the values given by Williams and Beaver are apparently seriously in error. Messinger (*8*) determined the heats of combustion of purified rubber, balata, and gutta-percha in an attempt to see if there were enough differences to throw light on their structural differences. He reports them to be the same within experimental errors and concludes that no deductions as to their respective structures may be





drawn from his work. His accuracy was not of the highest, the individual values for rubber varying about 4 per cent.

Apparatus

The calorimeter used in the present work was made with an adiabatic jacket of the type suggested by Daniels (*3*). The calorimeter thermometer was calibrated by the Bureau of

Standards and was readable to thousandths of a degree Centigrade. The jacket thermometer was carefully standardized against the calorimeter thermometer.

In burning materials containing less than 4 per cent sulfur, spun-nickel linings were used in the bomb, while for greater amounts of sulfur linings made of fused silica were employed. The standardization of the apparatus was checked by determining the heat of combustion of specially purified benzoic acid supplied by the Bureau of Standards.

Sulfur-Rubber System

A sample of 50 pounds (22.7 kg.) of smoked sheets was broken down, thoroughly blended, and set aside for the work. Four rubber-sulfur compounds were mixed and heats of combustion determined on the unvulcanized mixtures. A blank determination was made on the smoked sheets.

Compound		Heat of Combustion
Rubber	Sulfur	
Parts	*Parts*	*Cal. per gram compd.*
100	..	10547
92	8	10055
82	18	9434
76	24	9061
68	32	8568

These values, when plotted against the percentage of sulfur, lie on a straight line, Figure 1, curve A.

Rubber-sulfur mixes were made on the mill in the usual manner. They were vulcanized between sheets of aluminum for 6 hours at 160° C. (320° F.) in the laboratory hydraulic press. Curtis, McPherson, and Scott (*2*) have shown that rubber-sulfur compounds when cured to this extent have less than 0.07 per cent free sulfur up to 14 per cent sulfur. From 14 to 32 per cent sulfur the value is somewhat higher, but for ordinary purposes the total amount of sulfur compounded may be considered to have become combined under the conditions of vulcanization.

Preliminary work showed that certain of the compounds were very susceptible to oxidation. When allowed to stand exposed to the atmosphere for a month, they gave heats of combustion as much as 400 calories per gram lower than that of a freshly cured sample. All samples, therefore, were vulcanized, kept overnight in a vacuum desiccator, and the heat of combustion determined the next day.

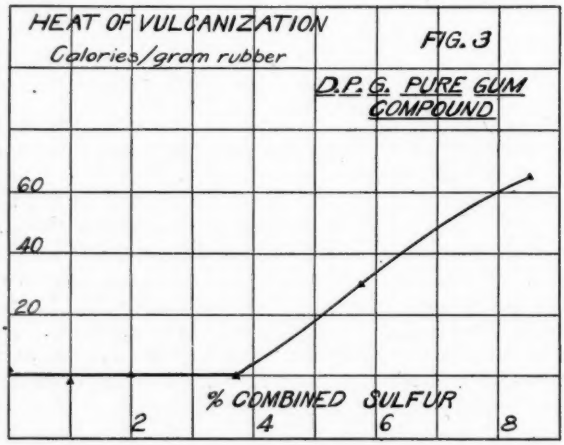
Compound		Heat of Combustion	Compound		Heat of Combustion
Rubber	Sulfur		Rubber	Sulfur	
Parts	*Parts*	*Cal. per gram compd.*	*Parts*	*Parts*	*Cal. per gram compd.*
100	..	10547	90	10	9849
98	2	10395	88	12	9693
96	4	10298	82	18	9275
94	6	10198	76	24	8811
92	8	9978	68	32	8268

These values are plotted as curve *B* in Figure 1 and give a fairly smooth curve. This curve coincides with curve *A* over the range of 0 to 6 per cent of sulfur and then falls below it

in a gradually increasing amount. The difference between the two curves is the heat of vulcanization and is calculated for nine points. All previous values have been given on the basis of a gram of the compound. In the last column they are converted to the basis of a gram of raw rubber.

Sulfur	Heat of Combustion		Heat of Vulcanization	
	Vulcanized	Unvulcanized	Per gram compd.	Per gram rubber
Per cent	*Cal.*	*Cal.*	*Cal.*	*Cal.*
0	0	10547	0	0
2	10395	10425	30	30
4	10298	10302	4	4
6	10198	10180	−18	−19
8	9978	10055	77	84
10	9849	9931	82	91
12	9693	9807	114	130
18	9275	9434	159	194
24	8811	9061	250	329
32	8268	8568	300	442

The heat of vulcanization per gram rubber is plotted against the per cent sulfur in Figure 2.



Soft Vulcanized Rubber

An accelerator speeds up the formation of soft vulcanized rubber and allows it to be produced with less combined sulfur. The following compound was mixed and cured: smoked sheets 600, zinc oxide 30, sulfur 60, and D.P.G. 4.5. Heats of combustion determinations were made. An unusually large amount of sulfur was used so that the soft-rubber formation could be completed and the hard-rubber reaction started. Heats of vulcanization are plotted against combined-sulfur values in Figure 3. The correct cure at the temperature used is approximately 20 minutes. At the 160-minute cure the hard-rubber reaction is well started and the resemblance of Figure 3 to the first part of Figure 2 is quite evident. The heat of vulcanization becomes evident at about 4 per cent combined sulfur. The use of an accelerator has apparently

allowed an earlier beginning of the hard-rubber reaction with its attendant evolution of heat.

Time of Vulcanization at 142° C.	Heat of Combustion	Heat of Vulcanization		Combined Sulfur on Rubber+ Sulfur	Tensile Strength 2 days O. B at 70° C.			
		Per gram compd.	Per gram rubber		New			
Minutes	*Cal. per gram*	*Cal.*	*Cal.*	*Per cent*	*Kg./ sq. cm.*	*Lbs./ sq. in.*	*Kg. per sq. cm.*	*Lbs. per sq. in.*
0	9516	..	..	...	...	...	...	..
10	9506	0	0	1.0	155.8	2213	66.5	945
20	9510	..	..	1.97	192.4	2733	103.8	1474
40	9515	..	..	3.66	240.5	2415	58.1	825
	Av. 9512							
80	9484	28	32	5.82	26.1	370	...	..
60	9456	56	65	8.50	24.2	345	...	..

The comparison of the physical properties of this compound with the thermochemical progress of the reaction is illustrated by Figure 4. The decrease in original tensile strength begins as the evolution of heat due to the reaction becomes apparent. The evolution of heat is associated with the formation of hard rubber and the decline of physical properties sets in when this becomes appreciable.

m-Dinitrobenzene

m-Dinitrobenzene is capable of vulcanizing rubber in the presence of litharge to give a material having a tensile strength of about 98.6 kg. per sq. cm. (1400 lbs. per sq. in.). This is nearly as good physically as the material produced by sulfur without the use of an organic accelerator. *m*-Dinitrobenzene apparently is capable of forming only soft vulcanized rubber. The reaction, therefore, offers a means of studying the formation of soft rubber without the complicating hard-rubber reaction being present. The following compound was mixed and cured: smoked sheets 600, litharge 60, and *m*-dinitrobenzene 18. Heats of combustion were determined on three cures and on the unvulcanized material.

Time of Cure at 145° C. (293° F.)	Heat of Combustion
Minutes	*Cal. per gram compd.*
Unvulcanized	9428
60	9430
120	9426
240	9428

It is quite evident that there is no apparent heat interchange in the vulcanization of rubber with *m*-dinitrobenzene.

Selenium

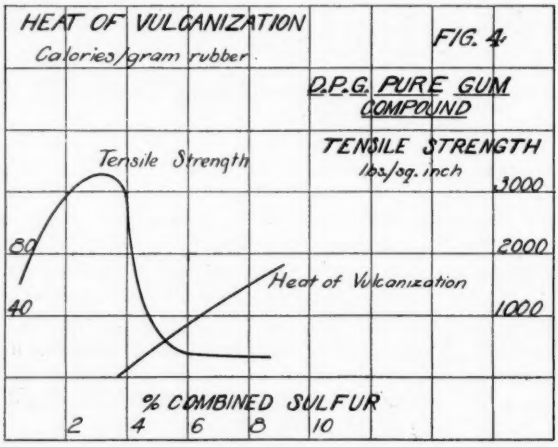
Selenium vulcanizes rubber in the presence of certain organic accelerators, giving a vulcanizate with many desirable properties. Apparently, it is also capable of forming only soft rubber. This reagent likewise allows isolation of the soft-rubber reaction for study.

The following compound was mixed and cured: smoked sheets 400, litharge 20, selenium 50, and *p*-nitrosodimethyl-

aniline 12. Heats of combustion were determined on both the vulcanized and unvulcanized material.

Time of Cure at 149° C. (300° F.) *Minutes*	Heat of Combustion *Cal. per gram compd.*
Unvulcanized	9004
60	8982
120	8986

To check this conclusively and give more definite evidence that selenium does not undergo the hard-rubber reaction, the following compound was mixed: smoked sheets 400, selenium 500, *p*-nitrosodimethylaniline 12, and litharge 20. This compound contains 125 per cent selenium on the rubber. It was cured 16 hours at 160° C. (320° F.). This is approximately sixty times the vulcanizing effect necessary to produce good, soft, vulcanized rubber from this mix. The product did not resemble hard rubber at all. Heats of combustion



determinations were made on the vulcanized and unvulcanized material.

	Heat of Combustion *Cal. per gram*
Unvulcanized	5037
Vulcanized	5045

It is quite evident that the vulcanization of rubber with selenium also does not involve any heat interchange.

Discussion

The curve illustrating the heat of vulcanization of rubber with sulfur in Figure 2 is quite striking. Apparently there is little or no heat interchange in the vulcanization of a rubber-sulfur mix until after about 6 per cent sulfur has combined. From this point to the complete formation of hard rubber there is a steadily increasing heat evolution. This evolution appears to be approximately propor-

tional to the amount of combined sulfur above 6 per cent. This quite agrees with the conclusions arrived at qualitatively by Perks, who found that the combination of rubber and sulfur was accompanied by a slight evolution of heat in the first stage of the reaction, followed by an energetic exothermic reaction. This latter reaction does not commence until 4 to 5 per cent sulfur has combined with the rubber. He, however, claimed a maximum heat effect at 21 per cent combined sulfur, which does not agree with the present work. The formation of hard rubber is accompanied by an evolution of 442 calories per gram of rubber. The significance of this high value may perhaps be best illustrated by the fact that if vulcanization of a hard rubber compound could be started and there were no heat lost in the process, the temperature would rise about 1000° C. or 1800° F. (specific heat = 0.4). It is well known that large masses of hard rubber compounded chiefly of rubber and sulfur explode with violence during vulcanization.

The average value for the heat of vulcanization of 10 calories per gram as calculated by Williams and Beaver at 10 per cent combined sulfur is apparently far below the new value. Their statement that there is an evolution of heat at the beginning of the reaction followed by a small absorption at the end seems to be the reverse of the present results.

The formation of soft vulcanized rubber and of ebonite seems to be two distinct and separate processes and very different thermochemically.

Literature Cited

(1) Bostrom, *Kolloidchem. Beihefte*, **24**, 467 (1928).
(2) Curtis, McPherson, and Scott, Bur. Standards, *Sci. Paper* **560**.
(3) Daniels, *J. Am. Chem. Soc.*, **38**, 473 (1916).
(4) Hock, *Kautschuk*, **1927**, 207.
(5) Kirchhof, *Gummi-Ztg.*, **39**, 892 (1925).
(6) Kirchhof and Matulke, *Ber.*, **57B**, 1266 (1924).
(7) Kirchhof and Wagner, *Gummi-Ztg.*, **39**, 357, 372 (1925).
(8) Messinger, *Trans. Inst. Rubber Ind.*, **5**, 71 (1929).
(9) Perks, *J. Soc. Chem. Ind.*, **45**, 142T (1926).
(10) Seidl, *Gummi-Ztg.*, **25**, 710, 748 (1911).
(11) Weber, "Chemistry of India Rubber," pp. 106, 114.
(12) Williams and Beaver, IND. ENG. CHEM., **15**, 255 (1923).

II—Vulcanization of Rubber with Nitro Compounds

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The Kjeldahl method for nitrogen analysis can be adapted to the determination of combined nitrogen in rubber vulcanized with nitro compounds. The combination of nitro compounds with rubber has been followed in several cases. Strong evidence is given that the vulcanization is a chemical reaction.

The density of rubber has been shown to change during vulcanization with dinitrobenzene. The change approximates the progress of the combination of the vulcanizing agent with rubber.

The vulcanization of rubber with dinitrobenzene and trinitrobenzene is monomolecular. A theory of the mechanism of the vulcanization is advanced.

The value of the stoichiometric method in estimating the molecular weight of rubber is discussed. Values of this constant are suggested by the data.

Nitro compounds appear to be incapable of producing hard rubber. The amount of combined reagent is only a small fraction of that required for ebonite formation.

SEVERAL years ago Ostromuislensky (*8*) showed that a number of organic materials possess the ability to vulcanize rubber. The vulcanization does not develop quite such good physical properties in the rubber as sulfur does, but there is no question that it does take place. Trinitrobenzene, *m*-dinitrobenzene, and benzoyl peroxide were shown to be the most satisfactory of the vulcanizing agents.

We have never been able to produce a material resembling ebonite by using the above materials as vulcanizing agents. This suggests that the reagents are capable of undergoing only the soft-rubber reaction. They fall, therefore, in the same class with selenium. This reaction offers a method of studying the formation of soft rubber without the complicating effect of the hard-rubber reaction. The vulcanization of selenium has been shown to be a chemical reaction and to follow the mass-action laws. Vulcanization of rubber with nitro compounds should follow the same course and throw more light on the mechanism of vulcanization.

Fisher and Gray (*3*) have investigated the vulcanization of rubber with dinitrobenzene, trinitrobenzene, and benzoyl peroxide. They have determined the unsaturation of the vulcanized rubber by the Kemp-Wijs method (*6*). Briefly, this consists of allowing the material to react for a definite length of time with an excess of iodine chloride. The excess is determined and the amount of iodine chloride absorbed is a measure of the unsaturation. They found that the rubber vulcanized with these materials had approximately the same degree of unsaturation as the unvulcanized rubber. They therefore concluded "that ordinary vulcanization is an unknown or undetermined type of change in the hydrocarbon involving no change in the unsaturation, and that the chemical union of sulfur is a secondary reaction producing a further change which, no doubt, gives properties that are very important in the manufacture of rubber goods but which is a change of degree only, not of kind."

Stevens (*11*) has also investigated the vulcanization of rubber with trinitrobenzene. He found that treating the acetone extract of the rubber with sodium hydroxide gave no red

coloration, indicating the absence of trinitrobenzene. This would imply that the trinitrobenzene had either been destroyed during vulcanization or had combined with the rubber and therefore could not be extracted with acetone.

Determination of Nitrogen in Vulcanized Rubber

If a chemical reaction does take place during vulcanization with nitro compounds, it is probably best followed by analysis. This may be followed, presumably, by determining the combined nitrogen. Since the amount of this nitrogen is small, the Dumas method for nitrogen determinations is not sensitive enough to be of value. The Kjeldahl method is very much more sensitive and is universally used for nitrogen determinations on certain types of materials. It is, however, a generally accepted belief that the method is unreliable in the case of compounds containing nitrogen linked to oxygen. Brinton, Schertz, Crockett, and Merkel (*1*) have attempted to adapt the Kjeldahl method to the determination of nitrogen in nitronaphthalenes. This was done by applying a correction factor, but obviously this method is useless for the present work. Investigation showed that the determinations of nitrogen in dinitrobenzene by the Kjeldahl method were low. The loss of nitrogen is due to the fact that the nitro compound slowly distilled out of the sulfuric acid during the heating and was lost before it could be attacked and absorbed. If the nitro compound was mixed into rubber and a nitrogen determination made on the mixture, excellent values were obtained. Apparently the presence of the rubber is sufficient to hold the nitro compound in the acid until it has been converted into a nonvolatile nitrogen-containing material.

A batch of smoked sheets was set aside for the work and the nitrogen content determined as follows: 0.498, 0.489, 0.468, 0.508, 0.477; average, 0.488 per cent.

Preliminary tests showed that dinitrobenzene and trinitrobenzene were soluble enough in acetone so that this solvent could be used to remove the free nitro compound from the rubber.

A series of cures were made of the following compounds:

	Compd. A	Compd. B	Compd. C
	Parts	*Parts*	*Parts*
Smoked sheets	600	600	600
Litharge	60	60	60
Dinitrobenzene	36	60	...
Trinitrobenzene	...	...	36
	Per cent	*Per cent*	*Per cent*
Rubber	86.2	83.3	86.2
Rubber hydrocarbon	80.1	77.5	80.1

Vulcanization was carried out between sheets of aluminum. Accurate timing was obtained by having the plates hot when the sample was inserted in the press. The samples were chilled in cold water on removal from the press and dried in a vacuum desiccator. The vulcanized samples were rolled thin on the mill, wrapped in extracted filter paper, and acetone-extracted for 16 hours. Preliminary results showed that

the extraction was complete in 8 hours. The samples were freed of solvent in the vacuum desiccator and analyzed for nitrogen. The values for combined nitrogen have been corrected for the crude-rubber content of the compound, the nitrogen content of the raw rubber, and then calculated to the rubber hydrocarbon basis, assuming that the raw rubber contained 93 per cent hydrocarbon.

Time of Cure	Combined Nitrogen 1	2	Av.	On Rubber	Corrected	On Rubber Hydrocarbon
Min.	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
			Compound A—145° C. (293° F.)			
10	0.512	0.492	0.502	0.582	0.094	0.103
20	0.814	0.785	0.800	0.928	0.440	0.473
30	1.072	1.058	1.065	1.246	0.758	0.816
45	1.211	1.264	1.238	1.437	0.949	1.020
60	1.230	1.266	1.248	1.448	0.960	1.033
75	1.282	1.278	1.280	1.485	0.997	1.072
105	1.243	1.236	1.240	1.440	0.952	1.023
240	1.190	0	1.190	1.382	0.894	0.962
			Compound B—132° C. (270° F.)			
15	0.512	0.474	0.493	0.592	0.104	0.112
30	0.670	0.670	0.670	0.804	0.316	0.340
45	0.809	0.812	0.811	0.973	0.485	0.522
60	0.935	0.943	0.939	1.128	0.640	0.688
75	1.012	1.036	1.024	1.230	0.742	0.797
90	1.038	1.082	1.060	1.272	0.784	0.843
240	1.240	1.218	1.229	1.475	0.987	1.061
			Compound C—129° C. (265° F.)			
5	0.946	0.963	0.954	1.105	0.517	0.664
10	1.090	1.158	1.124	1.303	0.815	0.877
15	1.196	1.198	1.197	1.389	0.901	0.970
20	1.236	1.213	1.225	1.422	0.934	1.004
30	1.255	1.268	1.261	1.463	0.975	1.048
40	1.249	1.310	1.280	1.485	0.997	1.071
			Compound C—124° C. (255° F.)			
5	0.729	0.720	0.724	0.840	0.352	0.379
10	1.008	1.032	1.020	1.182	0.694	0.747
15	1.140	1.140	1.140	1.322	0.834	0.897
20	1.192	1.228	1.210	1.403	0.915	0.985
60	1.212	1.230	1.221	1.418	0.930	1.000
80	1.240	1.290	1.265	1.468	0.980	1.052

The above figures indicate that there is a definite end point to the reaction in each case. It is interesting to compare the maximum values for combined nitrogen due to the nitro compound in each of the above cases. The amount available for combination is also tabulated.

Compound	Temp. of Cure ° C.	° F.	Nitrogen Available	End value
			Per cent	*Per cent*
		Cured with dinitrobenzene		
A	145	293	1.075	1.072
B	132	270	1.790	1.061
		Cured with trinitrobenzene		
C	129	265	1.271	1.071
C	124	255	1.271	1.052

It is significant that the end values check each other so closely, when in three cases there was an appreciable excess of vulcanizing agent. In addition to this, the curing temperatures covered a wide range and two different nitro compounds were used.

Changes in Density during Vulcanization

While the chemical analyses leave no doubt that the vulcanization with nitro compounds is a chemical reaction, it is

desirable to confirm the progress of vulcanization independently. Many chemical reactions involve a change in density of the mixture of reactants. Curtis, McPherson, and Scott (*2*) have shown that hard rubber has a density several per cent different from that of raw rubber. Soft vulcanized rubber has only about one-thirtieth the combined sulfur of hard rubber. In spite of this it was hoped that there would be enough change in density of rubber during vulcanization with dinitrobenzene so that the course of the reaction could be followed.

Samples of B cured for various lengths of time were freed of air by immersing in water and evacuating for 30 minutes in a vacuum desiccator. Densities were determined in a pycnometer in a thermostat maintained at 25° C.

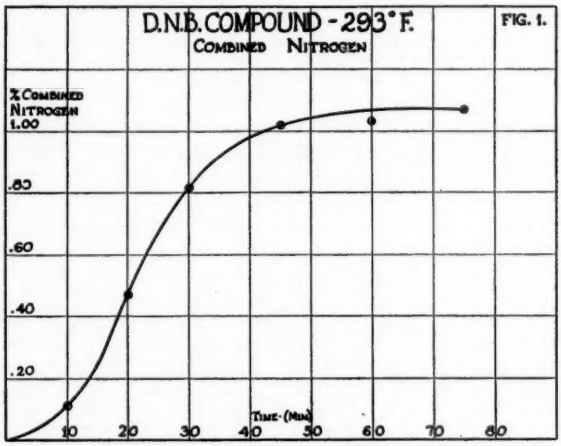


FIG. 1.

CURE AT 132° C. (270° F.) *Minutes*	DENSITY AT 25° C.
Unvulcanized	1.0289
15	1.0267
30	1.0292
45	1.0337
60	1.0463
240	1.0419

The density determinations were not of the accuracy hoped for. The pycnometer used has several errors inherent in the design. The above data, however, give a definite qualitative indication of the trend of the reaction; they leave no doubt that a definite change in density occurs and supplements the evidence of a chemical reaction as furnished by nitrogen analyses.

Kinetics of Vulcanization Reaction

From the nature of the vulcanization of rubber with nitro compounds, it should be classed as a second-order reaction. If the reaction is

Rubber + nitro compound = vulcanized rubber

clearly two distinct materials react and, as far as is known, in single molecular proportions. If they reacted in more than single molecular proportions, the order of the reaction would be increased and with it the difficulty of a mathematical analysis. If the above reasoning is correct, the reaction may be represented as follows:

$$A + B = C$$

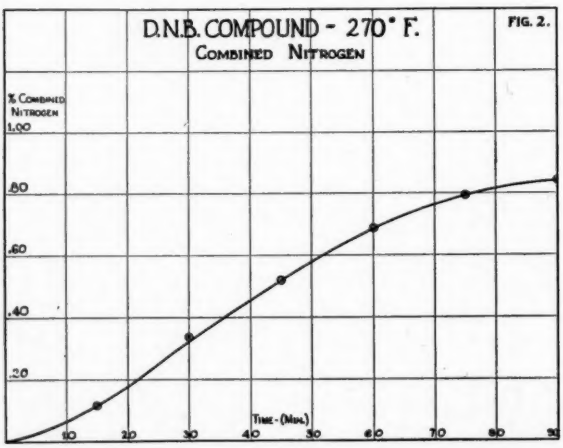
and the progress of the reaction may be expressed by the conventional second-order equation

$$\frac{dx}{dt} = K(a - x)(b - x)$$

which integrates to

$$K = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)}$$

where t = time
x = concentration of C at time t
a = original concentration of A
b = original concentration of B
K = specific reaction rate constant



In the special case in which the value of b is over ten times that of a, the value of $(b - x)$ changes little during the reaction and may be considered to be constant. This constant may be incorporated in the value of K and the equation becomes first order.

This equation, of course, integrates to

$$K = \frac{2.303}{t} \log \frac{a}{a - x}$$

In the cases under consideration the values of a and b seem to be of the same order of magnitude and the second-order equation should hold. All attempts to fit the data to the equation failed. Two intermediate points, together with the initial and final values, determine the order of a reaction. Curves representing equations of the first, second, and third

order were plotted through a point near the center of the datum curves. The first-order curves fitted the data most closely. Specific-reaction-rate constants have been calculated by means of that equation.

Compd. A 145° C. (293° F.)		Compd. B 132° C. (270° F.)		Compd. C 129° C. (265° F.)		Compd. C 124° C. (255° F.)	
Min.	$K \times 10^4$	*Min.*	$K \times 10^4$	*Min.*	$K \times 10^4$	*Min.*	$K \times 10^4$
10	99	15	73.7	5	1463	5	894
20	292	30	129.2	10	1702	10	1233
30	475	45	150.8	15	1538	15	1272
45	673	60	174.5	20	1383	20	1354
60	678	75	186.0	30	1271	60	496
		90	176.1				

The constants as calculated above have a very decided tendency to increase as the reaction progresses. Inspection of the curves gives a plausible reason for this. The first part of the curves, especially those for the dinitrobenzene compounds, is reversed, indicating a disturbing effect at that point. The nature of the disturbance is a matter for speculation, but its presence must be recognized and correction made for it in order to obtain entirely satisfactory constants. The effect of this factor is to delay the real start of the reaction. Allowance may be made for this by subtracting a definite amount of time from the observed values to give an apparent one. Values of this correction may be estimated empirically. The specific-reaction-rate constants have been recalculated by this method.

Compd. A 145° C. (293° F.) Cor. −13 min.		Compd. B 132° C. (270° F.) Cor. −10 min.		Compd. C 129° C. (265° F.) Cor. −1 min.		Compd. C 124° C. (255° F.) Cor. −2 min.	
Min.	$K \times 10^4$	*Min.*	$K \times 10^4$	*Min.*	$K \times 10^4$	*Min.*	$K \times 10^4$
10	0	15	221	5	1832	5	1493
20	835	30	193	10	1890	10	1542
30	840	45	194	15	1670	15	1465
45	930	60	209	20	1455	20	1532
60	867	75	214	30	1320		
		90	198				
Av.	868		205		1638		1508

A less empirical method of evaluating time corrections is to plot values of log $(a/a - x)$ against time. The best straight line through the points cuts the axis at a definite value of time, which is equal to the desired correction.

The use of the above time corrections gives values for K that do not vary seriously. It is interesting to note that the trinitrobenzene compounds have practically no time correction and the dinitrobenzene compounds have an appreciable one, and further that it is approximately the same for the two rubber compounds (A and B).

It is desirable to supplement the above constants by calculating them in a manner not involving time corrections and at the same time establish the validity of the above constants. Such a method involves the so-called point-to-point equation. If the first-order equation be integrated between limits, this equation is obtained.

$$K = \frac{2.303}{t_2 - t_1} \log \frac{(a - x_1)}{(a - x_2)}$$

The necessity for using a time correction is eliminated by this equation. Values of K have been calculated for all possible combinations of time in compound B, which was chosen because its curve had the largest number of measured points.

No.	T_2	T_1	$K \times 10^4$	No.	T_2	T_1	$K \times 10^4$
1	30	15	169	9	75	30	224
2	45	30	194	10	75	15	214
3	45	15	189	11	90	75	124
4	60	45	245	12	90	60	179
5	60	30	217	13	90	45	201
6	60	15	208	14	90	30	200
7	75	60	231	15	90	15	197
8	75	45	235			Average	202

The average of these fifteen values is less than 2 per cent different from the average value calculated by the use of empirical time correction. The average of the directly calculated values is over 25 per cent lower and the values in themselves vary seriously and directionally.

The agreement of the above values with each other is very satisfactory when it is considered how sensitive such values are to experimental error. For example, constant No. 11 is farthest from the average and 40 per cent below it. If the value for the nitrogen analysis is altered by 0.02 per cent, the value for K is increased 100 per cent and is over 20 per cent higher than the average. The agreement of the constants calculated by the use of the point-to-point equation leaves little doubt that the first-order equation interprets the data.

Mechanism of Vulcanization

It has been proved that the vulcanization of rubber with *m*-dinitrobenzene and trinitrobenzene follows the first-order law. This is contrary to preconceived ideas and requires explanation. It was assumed that, since the two substances react with one another to form a compound or compounds and are present originally in approximately the proportions in which they combine, the reaction should be at least of the second order.

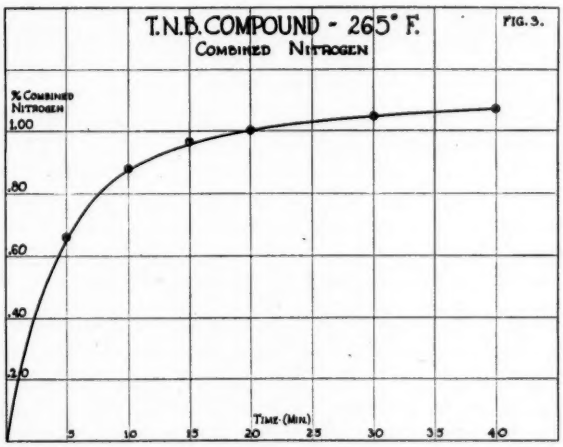
Frequently reactions occur in steps. Each of the step reactions has its own reaction rate, and if one of these rates is much smaller than the others, it will control the series of reactions. In that case measurements of the progress of the whole reaction will really be of this particular part of the transformation.

In the present case the vulcanization reaction is measured by the combined nitrogen remaining in the rubber after acetone extraction. If the total reaction thus measured consists of more than one reaction, the kinetics may be satisfactorily explained. The most obvious theory is that the rubber hydrocarbon and the nitro compound unite to form a rather loose molecular compound, which is then converted by continued heating to real vulcanized rubber. The course of the reaction would then be represented by the following two equations:

Rubber + nitro compound ⟶ (rubber)(nitro compound) (1)
(Rubber)(nitro compound) ⟶ vulcanized rubber (2)

The first reaction may be quite rapid and the second one relatively slow. The slower one would therefore more or less completely mask the first reaction. This second reaction, since only one molecular species is the starting point, would be monomolecular and thus of the first order. This would correspond completely to the experimental results. Since the progress of the first reaction is not made evident by the analyses, it seems probable that the product of the reaction, the loose molecular compound, is decomposed by the extraction of the material with boiling acetone. If it were not, the nitrogen values should be constant.

The addition of nitro compounds to hydrocarbons to form more or less stable molecular compounds is well known. Picric acid, for example, forms a double compound with benzene,



naphthalene, phenanthrene, anthracene, etc. The molecular compound with benzene, although crystallizing easily from organic solvents, is decomposed into its two constituents by oxygenated solvents such as water, an indication of the looseness of combination. This decomposition may be similar to the one that occurs when a loose molecular compound of rubber and nitro compound is treated with hot acetone during the extraction. The use of a solvent which contains no oxygen for the extraction might give entirely different values for combined nitrogen.

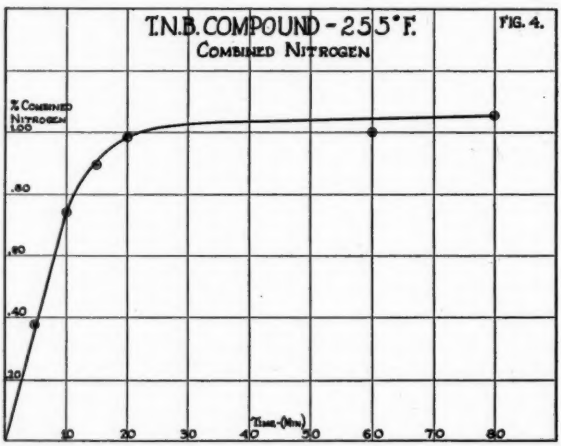
If this were the mechanism of the vulcanization and the first reaction were slow enough to affect the rate of the second, the kinetics of consecutive reactions would be applicable. The dinitrobenzene curves are S-shaped and have an appreciable time correction, while the trinitrobenzene curves have practically none. Compounds with three nitro groups form these double compounds with hydrocarbons rapidly

and the compounds thus formed are relatively stable. Compounds with only two nitro groups give double compounds that are not so stable. An example of this is the double compound of picric acid and naphthalene, which is stable and crystallizes easily. The double compound of naphthalene and dinitrobenzene cannot be isolated and its existence can be proved only by a phase diagram (*10*).

There seems to be considerable evidence that the vulcanization of rubber with nitro compounds takes place in two steps and that the second step is the slower and the one measured in the present paper.

Molecular Weight of Rubber

The molecular weight of rubber has been the subject of much speculation. Gladstone and Hibbert (*4*) in 1889 estimated it to be about 2000. Hinrichsen and Kindscher (*5*)



have obtained better data by measuring the depressing effect of rubber on the freezing point of benzene. They corrected for the presence of resins, etc., and found a value of 3173. The latest and most satisfactory cryoscopic determination is by Pummerer (*9*), who, by using the depression of the freezing point of menthol, obtained values of 3400 to 3600.

Knoepelin (*7*) has measured the osmotic pressure of dilute solutions of rubber in benzene and from it has calculated the molecular weight to be 30,000 to 50,000.

The foregoing data on the chemical reaction between nitro compounds and rubber give an entirely independent method of estimating minimum molecular-weight values. If we assume that during vulcanization one molecule of nitro compound reacts with one molecule of rubber, a simple stoichiometric calculation gives us the molecular weight. In the case of dinitrobenzene this value is 2630, and with trinitrobenzene it becomes 3940. These values are of the same mag-

nitude as those found by cryoscopic determinations, but they are quite different from each other. Obviously, since in each case the combined nitrogens are of the same value, the calculated molecular weight is proportional to the number of nitro groups. This would imply that the nitro group is the essential component of the vulcanizing agent and that one molecule each of the reagent and rubber is not involved in the final product. If each nitro group in the reagent is capable of vulcanizing a molecule of rubber, its molecular weight would be 1315. Another alternative in an attempt to reconcile the two values with each other is to assume that six or a multiple of six nitro groups are required. The molecular weight would then be 7880 or a multiple of it. The third alternative is to assume that neither a single molecule of the nitro compound nor a single molecule of rubber is a part of the final product. This, of course, leads to a variety of conclusions. More data are needed before the matter can be settled, but it is very desirable to indicate the possibility of solving this much-discussed problem by stoichiometric methods.

Discussion

The above results allow conclusions to be drawn that are contrary to those of Fisher and Gray (*3*). The inference from their unsaturation determinations is that no measurable combination of nitro compound with rubber takes place. In sulfur vulcanization unsaturation measurements clearly indicate the progress of a chemical reaction. The present investigation shows that a chemical reaction does take place when rubber is vulcanized with di- and trinitrobenzene, and that the reaction follows the conventional kinetic laws.

Rubber vulcanized with sulfur is unable to have the chemically combined sulfur removed without destroying the rubber molecule. The chemical combination of nitro compounds with rubber is not so vigorous as sulfur vulcanization, as is evidenced by the inability of nitro compounds to form hard rubber. This union of rubber and nitro compounds may be so weak that the treatment of the product with iodine chloride displaces the nitro compound. This would account for the anomalous results of Fisher and Gray. There is some indication that the compound of dinitrobenzene and rubber is capable of being broken down by heat. Compound *A* reaches a maximum value for combined nitrogen and then the amount slowly decreases with continued heating. It may be that heating for a long time at curing temperatures tends to convert some of the protein to acetone-soluble material and thus cause a decrease in combined nitrogen.

The investigation obviously leaves many unsettled points of interest and further work is in progress in an attempt to solve these problems.

Literature Cited

(1) Brinton, Schertz, Crockett, and Merkel, J. IND. ENG. CHEM., **13**, 636 (1921).

(2) Curtis, McPherson, and Scott, Bur. Standards, *Sci. Paper* **560**.
(3) Fisher and Gray, IND. ENG. CHEM., **20**, 294 (1928).
(4) Gladstone and Hibbert, *J. Chem. Soc.*, **56**, 1207a (1889).
(5) Hinrichsen and Kindscher, *Ber.*, **42**, 4329 (1909).
(6) Kemp, IND. ENG. CHEM., **19**, 531 (1927).
(7) Knoepelin, *Kautschuk*, **236** (1924).
(8) Ostromuislensky, *J. Soc. Chem. Ind.*, **35**, 59, 396 (1916); *India Rubber World*, **80**, 55 (1929).
(9) Pummerer, *Z. Elektrochem.*, **34**, 664 (1928).
(10) Skau, *J. Am. Chem. Soc.*, **52**, 945 (1930).
(11) Stevens, *J. Soc. Chem. Ind.*, **36**, 107 (1917).

III—Kinetics of Vulcanization of Rubber with Sulfur and Selenium

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A procedure for the determination of combined selenium in rubber has been evolved. The rate of combination of selenium and rubber has been ascertained under certain conditions and shown to follow a first-order equation.

A minimum value for the molecular weight of rubber has been estimated.

The formation of hard rubber under chosen experimental conditions has been put on a mathematical basis and has been shown to follow a second-order reaction.

The soft- and hard-rubber reactions have been shown qualitatively to be successive reactions and the function of accelerators has been discussed.

The theory explains the anomalous results obtained by previous investigators.

THERE have been a great many attempts to explain the rate of combination of sulfur with rubber, but each one has been unsatisfactory from some viewpoint. Weber (*13*) obtained a series of irregular curves connecting combined-sulfur determinations with time of vulcanization. He concluded that the "kinks" in these curves represented definite compounds of rubber and sulfur, intermediate between raw rubber and $(C_5H_8S)_x$ hard rubber.

The presence of these breaks in the vulcanization curve has been refuted by a number of subsequent investigators and shown to have been due to experimental errors. Ostwald (*7*) claimed that the relation between combined sulfur and time of cure was a power function. Since the rate of combination was expressible as a logarithmic function, it was claimed to be an adsorption process. He also claimed that there was no definite end point to the combination of rubber with sulfur. Spence and Young (*11*) and other investigators have adequately shown that there is a definite end point to the chemical

reaction between sulfur and rubber. This end point occurs when 47.1 parts of sulfur have combined with 100 parts of rubber hydrocarbon. This corresponds to the compound $(C_5H_8S)_x$. Spence and Young (*10*) and Fol and van Heurn (*2*) have found a straight-line relationship between the combined sulfur and time of vulcanization under the specific conditions of their experiments. The relationship $X/t = K$ was deduced where X = amount of combined sulfur, t = time of vulcanization, and K the rate constant of the reaction. This relation, of course, could not hold over an indefinite range and has not been explained on any chemical basis. Skellon (*9*) and more recently Glancy, Wright, and Oon (*3*) have studied hard-rubber formation and obtained S-shaped curves for the course of the reaction. Van Iterson (*4*) has claimed that this is indicative of an autocatalytic process, but he does not support his ideas by any plausible chemical theory. The kinetic laws of chemical reactions are, of course, well known, but attempts to apply them to vulcanization have hitherto been unsuccessful.

Theory

It may be assumed as a hypothesis that in the vulcanization of rubber two distinct and separate reactions take place, the formation of soft vulcanized rubber and the formation of hard rubber or ebonite $(C_5H_8S)_x$. (See Part IV) Selenium apparently only undergoes the soft-rubber reaction, since we have never been able to produce a material with this reagent at all resembling ebonite. If a kinetic study is made of rubber vulcanization with selenium with this principle in mind, a clearer understanding of the process with sulfur may be reached.

Vulcanization of Rubber by Selenium

The simplest type of vulcanization is that with selenium alone. If, as has been postulated, such vulcanization results in the formation of soft rubber only, there is no complicating hard-rubber reaction occurring simultaneously. The solubility of selenium in rubber at vulcanizing temperatures has been estimated by Williams (*14*) to be 0.5 per cent. Presumably the only selenium engaged in the vulcanization is the dissolved material. If there is a large excess of selenium present so that the rubber is always saturated with it, this amount will be constant and will give a reaction occurring in a homogeneous medium. There is little reason to believe that the solubility of selenium is altered appreciably during the course of the reaction, since the end product has a low coefficient of vulcanization. The solubility of sulfur in rubber is little affected by large changes in the coefficient of vulcanization (*5*, *12*). The equation governing the vulcanization of rubber by selenium should, therefore, be of the first order.

$$\frac{dx}{dt} = K(S - x)$$

where t = time
x = combined selenium
S = original amount of rubber which is equivalent to final amount of combined selenium
K = specific-reaction-rate constant

The specific-reaction-rate constant has included in it the solubility value for selenium in rubber, which is constant for any one temperature.

Selenium Determinations

The quantitative determination of total and combined selenium in rubber compounds offers considerable difficulty. Selenium reacts chemically quite differently from sulfur and has not the same solubility in various reagents. Preliminary work by the author on these methods has been reported previously (*1*) in connection with other studies on selenium.

TOTAL SELENIUM—The determination of total selenium in rubber was attempted by using various modifications of the fusion methods for sulfur to render the selenium soluble. Nitric acid digestions were also tried, but in each case, owing to the volatility of selenium compounds, low values were obtained. It was necessary, therefore, to resort to the use of the Carius method for converting selenium quantitatively to a soluble form. The element is normally determined gravimetrically, but since the use of a Carius tube limits the sample to 0.2 gram, a more sensitive method was required. The volumetric procedure of Norris and Fay (*6*) was adapted. The method finally evolved is as follows:

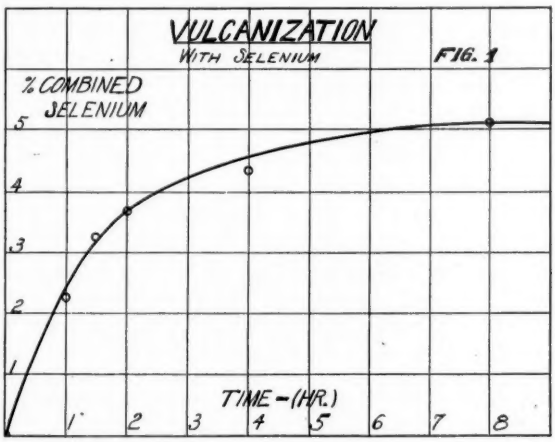
A 0.2-gram sample and 15 cc. of fuming nitric acid are sealed in a Carius tube and heated 2 hours at 235° C. When cool, the contents are washed into a beaker and evaporated to dryness on the water bath. Distilled water (10 cc.) is added and the mixture again evaporated to dryness to remove any remaining nitric acid. Fifty cubic centimeters of distilled water and 10 cc. of hydrochloric acid (sp. gr. 1.2) are added and an excess of 0.03 *N* sodium thiosulfate is run in. After standing 10 minutes, the excess thiosulfate is determined by titration with 0.03 *N* iodine, using starch as an indicator.

1 cc. 0.03 *N* $Na_2S_2O_3$ = 0.000594 gram selenium

COMBINED SELENIUM—Free selenium (gray) in a rubber compound is not soluble in the reagents normally used for extracting free sulfur. Long boiling of the rubber sample with aqueous potassium cyanide dissolves most of the free selenium, but the extraction is not complete. The subsequent determination of selenium in the extract is quite disagreeable on account of the large quantities of hydrocyanic acid evolved. Free selenium is soluble in Budde mixture. The selenium bromide thus formed attacks the rubber, however, adding to the remaining double bonds and increasing the combined selenium so that the method cannot be used directly. By forming the nitrosite of the rubber before dissolving out the free selenium, the unsaturation is eliminated and the selenium bromide can no longer react with the rubber after its forma-

tion. The combined selenium may be determined in the residue from the extraction by the method used for total selenium. The following method summarizes the results of the experiments:

A 0.2-gram sample is refluxed 2 hours with 50 cc. of carbon tetrachloride. The mixture is chilled by surrounding the flask with ice. Oxides of nitrogen, prepared by dropping nitric acid (sp. gr. 1.31) on arsenious oxide heated in the water bath, are bubbled through the mixture for 2 hours. It is desirable to free the gases of nitric acid and water by passing them through a chilled trap before they enter the mixture. The mixture is allowed to stand 16 hours at 0° C. to complete the formation of the nitrosite and then the oxides of nitrogen are removed by suction. Seventy-five cubic centimeters of Budde mixture (500 cc. CCl_4, 3 cc. bromine, 0.5 gram iodine) are added and the mixture is allowed to stand overnight in a dark place. An equal volume of alcohol is added and after 5 minutes the solid material is filtered off and washed with a mixture of equal volumes of



carbon tetrachloride and alcohol. The precipitate is dried at 80° C., placed in a Carius tube with nitric acid, and the combined selenium determined as in the method for total selenium.

Kinetics

The following compound was mixed and vulcanized in the laboratory press for various lengths of time at 148.8° C. (300° F.): smoked sheets 400, zinc oxide 20, selenium (gray) 500, and *p*-nitrosodimethylaniline 12 grams. The samples were only 0.070 inch (1.78 mm.) thick, so the temperature lag was believed to be negligible. The samples were ground to pass a 20-mesh sieve and combined selenium determined. A check determination for total selenium was made on the 4-hour cure to make sure that there had been no serious loss of selenium during vulcanization. The determinations of combined selenium were as follows:

Time of Cure	Selenium on Compound	Selenium Coefficient of Vulcanization
Hours	*Per cent*	
1	0.98	2.28
1.5	1.39	3.24
2	1.59	3.71
4	1.87	4.36
8	2.19	5.10

The first-order equation

$$\frac{dx}{dt} = K(S - x)$$

integrates to

$$Kt = \ln \frac{S}{S - x}$$

$$K = \frac{2.303}{t} \log \frac{S}{S - x}$$

From the shape of the curve in Figure 1 it is apparent that after 8 hours' vulcanization the reaction is practically complete. The value of S may therefore be assumed to be 5.10 per cent. Values for the specific-reaction-rate constant may then be calculated for the several times of cure. It is obvious that the units of S are of no consequence since they cancel in the formula.

Time of Cure	K
Hours	
1.0	0.596
1.5	0.673
2.0	0.652
4.0	0.484

These are quite satisfactory values for a specific-reaction-rate constant, since the reaction was about 50 per cent complete at 1.0 hour. The errors in calculating the constant are magnified as the value of x becomes large. To illustrate this, if an average of the first three constants is used to calculate the analytical values required to give this constant, the moderate deviation of the analysis is apparent. If $K = 0.640$

$$\frac{2.303}{t} \log \frac{S}{S - x} = 0.640$$

and solving for values of x for different times of t

Time of Cure	Combined Selenium	
	Calcd.	Found
Hours	*Per cent*	*Per cent*
1.0	1.03	0.98
1.5	1.35	1.39
2.0	1.58	1.59
4.0	2.02	1.87
8.0	2.18	2.19

The data indicate that the vulcanization of rubber by selenium follows the course of a first-order reaction and is therefore not complicated by any side reactions. The maximum coefficient of vulcanization obtainable with selenium is apparently about 5.1 per cent. This corresponds to a sulfur coefficient of 2.04 per cent. A large number of attempts have been made to produce ebonite by vulcanizing rubber with

selenium and an accelerator for long periods of time at high temperatures. In every case a soft-rubber product only was obtained. It would appear that selenium, being less active chemically than sulfur, undergoes only the soft-rubber reaction.

Molecular Weight of Rubber

Numerous attempts have been made to estimate the molecular weight of rubber. In the methods previously used the error is large for substances of high molecular weight. By stoichiometric means we may estimate a submultiple of the molecular weight from the above data.

Since 5.1 per cent selenium combines with rubber to form a stable compound, if only one atom of the metal combined with a molecule of rubber the minimum molecular weight would be 1560. This corresponds to 23 isoprene molecules. It is probable, however, that the rubber is a long-chain molecule. In this event the most reactive double bonds—the ones that take part in the soft-rubber reaction—would be on the ends of the chain. This would allow two selenium atoms to react with one molecule of rubber to form soft rubber. This doubles the previously estimated minimum molecular weight which becomes equal to 3120 or 46 isoprene molecules. Roberts and Mair (*8*) have recently studied the oxidation of rubber with hydrogen peroxide. They found that there was one molecule of carbon dioxide evolved for each 45 carbon atoms. This would correspond to a minimum molecular weight of 612 or 9 isoprene molecules, a value which happens to be a submultiple of the above.

Hard-Rubber Reaction

In a study of the hard-rubber reaction the soft-rubber reaction can be disregarded as a first approximation. As was shown above, when the reaction is complete the combined sulfur in the soft rubber would be only about 5 per cent of the total. At 170° C. the solubility of sulfur in rubber is more than 30 per cent and increases rapidly with an increase in combined sulfur, so that the hard-rubber reaction can take place in a one-phase homogeneous system. The corresponding equations should be applicable. The reaction should be of the second order if the theoretical amount of sulfur were used.

$$\frac{dy}{dt} = K(S - y)(R - y)$$

where y = amount of hard rubber formed or amount of combined sulfur
S = concentration of sulfur originally present
R = concentration of rubber originally present
t = time
K = specific reaction rate

All quantities are on a molal basis.
The equation integrates to

$$Kt = \frac{2.303}{S - R} \log \frac{R\,(S - y)}{S\,(R - y)} + C$$

C is the constant of integration, but we know from our given condition that when $t = 0$, $y = 0$, in which event $C = 0$. If original conditions can be so controlled that $S = R$, the equation simplifies considerably and becomes

$$KtS = \frac{y}{S - y}$$

If f be the fraction converted (y/S), the equation can be put in a much better form for use:

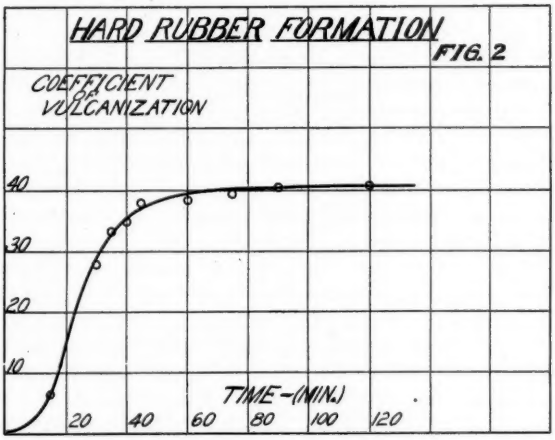
$$KtS = \frac{f}{1 - f}$$

The condition assumed (that $R = S$) is, of course, met when the theoretical quantities of rubber and sulfur required to form hard rubber are used (32 parts sulfur and 68 parts rubber). Glancy, Wright, and Oon (*3*) have met this condition practically by mixing 30 parts of sulfur with 70 parts of rubber and various accelerators. The difference between these quantities and the theoretical proportion is probably within experimental error.

In the calculation of specific-reaction-rate constants, time values are used. It is very difficult experimentally to establish the exact instant when a reaction is starting under controlled conditions. In a reaction occurring in a solvent, an appreciable time must elapse before a homogeneous solution and uniform concentration are obtained. In the hot vulcanization of rubber a certain amount of time must elapse before the reactants have been brought to the elevated temperature and the reaction started on its normal course. The higher the temperature the greater is this lag. In other words, a reaction probably does not start under controlled conditions at the time recorded in the data and all values of time are subject to a correction to place them on a true basis. The magnitude of the correction may be greater than is ordinarily supposed, but it can be estimated with a fair degree of accuracy. If values of $f/1 - f$ for the above reaction are plotted against time, the points should fall on a straight line. If there were no time corrections, this line should pass through the origin, but if there is a time correction the line cuts the horizontal axis. This point is the true starting time of the reaction and the recorded values of time should be corrected accordingly. Using these corrected times, uniform values of K should be obtained. Glancy, Wright, and Oon (*3*) determined the combined-sulfur curves for five compounds varying only the accelerator used. The compounds contained 70 parts of rubber and 30 parts of sulfur. The accelerators were (1) no accelerator, (2) 2.00 per cent diphenylguanidine, (3) 2.00 per cent ethylidene aniline, (4) 2.00 per cent hexamethylenetetramine, and (5) 1.00 per cent tetramethylthi-

uramdisulfide. The curve for (1) is plotted in Figure 2 as an example of the course of the reaction.

Percentages are calculated on the rubber. Plots were made of $f/1 - f$ against time for each of these compounds and the time corrections thus determined: (1) 21, (2) 8, (3) 2, (4) 9, and (5) 10 minutes. These values were used to give the corrected times. From them specific-reaction-rate constants were calculated for each compound. Since a large number of points on the curve were taken near the end of the reaction, some of the data are not so suitable as they might be. In the fraction $f/1 - f$ when f is large, small errors of f are multiplied many times in evaluating the fraction. The points where f is smaller are quite satisfactory.



Temperature = 170° C.

Compd. 1		Compd. 2		Compd. 3		Compd. 4		Compd. 5	
Min.	*K*	*Min.*	*K*	*Min.*	*K*	*Min.*	*K*	*Min.*	*K*
30	0.200	10	0.600	15	0.228	15	0.180	15	0.358
35	0.235	15	0.630	30	0.275	30	0.260	30	0.412
40	0.216	30	0.737	45	0.335	45	0.186	45	0.392
45	0.286	45	0.572	60	0.281	60	0.187		
60	0.203			75	0.258	75	0.187		
75	0.195					90	0.181		
90	0.198					120	0.152		
120	0.209								
Av.	0.218		0.635		0.287		0.190		0.387

The constants are very consistent and would indicate that the vulcanization of rubber to give ebonite is a second-order reaction. The least satisfactory set of constants is for compound 2, but in this case the reaction was 70 per cent complete at a corrected time of 2 minutes. In spite of the errors introduced, and the sensitivity of constants to these errors, the variation is not large.

The previous assumption was that the hard and soft rubber reactions occurred simultaneously, and that they probably both started at the same time. If they did, experimental conditions are nearly enough standardized so that the time corrections, which then should represent a heating lag, would be

constant. This is far from being the case, since the corrections vary from 2 to 21 minutes. The largest time correction is applied to the rubber-sulfur mix which contains no accelerator. The relative action of the other accelerators at 170° C. cannot be predicted from their accelerating value at ordinary temperatures, since their activities are undoubtedly different functions of temperature. The data, therefore, imply that the reactions of vulcanization are successive or consecutive rather than simultaneous. In a single molecule the soft-rubber reaction must be completed before the sulfur reacts to form hard rubber. Of course, in the whole mass, since all molecules do not react instantly, both reactions are proceeding at the same time, but in any one molecule they are successive. The above kinetic calculations, by introducing the time correction, disregard the soft rubber reaction.

The constants thus calculated for the hard-rubber formation are very interesting. The stocks containing hexamethylenetetramine and ethylidene aniline as accelerators give values for K that are essentially the same as that for the pure rubber-sulfur mix. The stocks containing tuads and diphenylguanidine have constants two and three times as large. This is not a large increase when it is considered that tuads, for example, may increase the rate of vulcanization to form soft rubber over fifty fold. The accelerators, then, do not vitally affect the rate of formation of hard rubber. They do, however, lower the time correction. In other words, they speed up the formation of soft rubber, which in turn is vulcanized to hard rubber at a fairly definite rate. The function of accelerators in hard-rubber manufacture is to accelerate the soft-rubber reaction so that the hard-rubber reaction may begin sooner. Of the two successive reactions, only the rate of the first is seriously alterable at the temperature under consideration.

Conclusion

These preliminary studies on the kinetics of vulcanization of rubber with sulfur and selenium give, it is believed, an insight into a much discussed but little understood subject. The work opens a new branch of rubber research and it is hoped that this and future work will throw much light on the mechanism of vulcanization. The concept of two separate reactions occurring in sulfur vulcanization seems substantiated and the evidence for their occurring consecutively suggests a mechanism of vulcanization that allows a rational interpretation of the apparently conflicting data in the literature. It is hoped that further studies will completely elucidate the mathematics of vulcanization reactions and allow the interpretation of all possible combinations of vulcanizing agents and accelerators.

Literature Cited

(1) Boggs and Follansbee, *Trans. Inst. Rubber Ind.*, **2**, 272 (1926).
(2) Fol and van Heurn, *Gummi-Ztg.*, **31**, 715 (1917).

(3) Glancy, Wright, and Oon, IND. ENG. CHEM., **18**, 73 (1926).
(4) Iterson, van, Comm. of Neth. Govt. Inst. VII, p. 251.
(5) Kelley and Ayers, IND. ENG. CHEM., **16**, 148 (1924).
(6) Norris and Fay, *Am. Chem. J.*, **18**, 704 (1895); **23**, 119 (1900).
(7) Ostwald, *Kolloid-Z.*, **6**, 136 (1910).
(8) Roberts and Mair, *J. Soc. Chem. Ind.*, **46**, 41T (1927).
(9) Skellon, *Kolloid-Z.*, **14**, 96 (1914).
(10) Spence and Young, *Chem.-Ztg.*, **36**, 1162 (1912).
(11) Spence and Young, *Ibid.*, **11**, 28 (1912); **13**, 265 (1913).
(12) Venable and Green, IND. ENG. CHEM., **14**, 319 (1922).
(13) Weber, "Chemistry of India Rubber," p. 85.
(14) Williams, IND. ENG. CHEM., **15**, 1019 (1923).

IV—A Theory of Vulcanization of Rubber

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A new theory has been advanced which, it is believed, explains completely the various phenomena connected with the vulcanization of rubber. It is entirely a chemical theory based on the existence of two separate and distinct rubber compounds, soft vulcanized rubber and ebonite. The theory explains satisfactorily the aging of rubber, the variation in combined sulfur at optimum cure caused by acceleration, the kinetics of vulcanization, the characteristics of various vulcanizing agents, the thermochemistry of vulcanization, the electrical properties of rubber, the reclaiming of rubber, and the Joule effect. A brief review and discussion of the phenomena and past theories of vulcanization have also been given.

THE vulcanization of rubber has always been a much discussed enigma. The progress of its practical application has been rapid and the quality of manufactured rubber articles steadily improved. The fundamental nature of vulcanization is still a matter of controversy and rubber technologists fail to agree on a single theory of vulcanization. Each group of adherents to a particular theory is unconvinced of the merits of a conflicting one. Furthermore, each main theory has its numerous variations in an attempt to explain facts discovered subsequent to the statement of the parent theory. Some theories are completely extinct and are of historical interest only. Others have been so altered that they but faintly resemble the original.

One cause of the difficulty in formulating a theory of vulcanization is the mass of conflicting data. There are many experiments recorded in the literature which are contradicted by others of apparently equal authenticity. Many unknown variables have entered into the data of the literature. To obtain a picture of the probable facts of vulcanization necessarily involves a certain amount of arbitrary selection of recorded data. The evolution of any theory is thus a difficult

process and a new one may be at once subjected to adverse criticism supported by literature references. None of the theories existing today explains all the known facts of vulcanization.

The theory here presented has been evolved in the belief that it agrees with many of the undisputed facts of vulcanization which were previously unexplained. No well-authenticated data have been found to be in conflict with it. A theory worthy of the name should evoke fresh ideas not implied by previous theories. The present one has led to the prediction of many such facts and they in turn strongly support the new theory.

Phenomena of Vulcanization

The entire physical properties of rubber are changed by vulcanization (*23*). Of the reagents used, sulfur is by far the most important. It is capable of producing both soft vulcanized rubber and hard rubber or ebonite. Soft rubber is essentially an elastic material, while hard rubber is thermoplastic (*11, 32, 68*). It is the formation of soft rubber that is of the greater technical importance, and this reaction is normally hastened by the use of accelerators. As a general rule, the greater the acceleration of vulcanization the smaller the amount of combined sulfur needed to produce optimum cure, the greater the physical properties developed, and the better the aging (*3, 8, 15*).

Vulcanized rubber on standing in the air usually shows a deterioration of physical properties (*57*), and this is accentuated by vulcanizing beyond the point of optimum cure. The ability of rubber to resist this deterioration may be improved, however, by the use of antioxidants (*36*), which are apparently negative catalysts of oxidation.

Chemically, crude rubber is composed chiefly of an unsaturated hydrocarbon (*47*) with the empirical formula $(C_5H_8)_x$. During vulcanization sulfur adds to its double bonds and ordinarily there is little or no substitution of sulfur for hydrogen. The ultimate product of this addition has one atom of sulfur for each isoprene unit (*65*). There has been a controversy of long standing over this point (*27, 29, 33, 50, 59, 67*), but it seems well established that the formula for ebonite is $(C_5H_8S)_x$. Under certain conditions substitution of hydrogen may take place to raise the sulfur content above that called for by the formula (*60*) but this is unusual and not a part of vulcanization.

Soft-rubber formation also involves the addition of sulfur to the rubber molecule, since Spence (*53*) showed that if the unsaturation were determined by means of bromine, the combined sulfur had reduced it by an equivalent amount.

The combined sulfur, contrary to some claims, cannot be removed from rubber without destruction of the molecule.

Certain compounds of sulfur, such as antimony sulfide (*14, 18, 35*), tetramethylthiuramdisulfide (*4, 5, 13*) and

selenium diethyldithiocarbamate (*37*) are also capable of vulcanizing rubber. The vulcanization involves the decomposition of the compound to provide the sulfur consumed, and in the latter case it is probable that selenium also combines.

Since vulcanization is a chemical reaction, its temperature coefficient should and does fall in the range called for by van't Hoff's law (*12*, *56*, *61*).

There has been some discussion as to whether the sulfur of vulcanization is in an adsorbed condition (*54*, *55*), but it has been shown that combined sulfur values are very definite (*30*, *52*, *58*).

The kinetics of vulcanization of rubber by sulfur has been the subject of much speculation. Weber's (*64*) series of irregular curves has been replaced by smooth ones, but the type varies with the investigator. Spence and Young (*56*) found a straight-line relationship and sponsored the corresponding equation. Skellon (*50*) and Glancy (*22*) found S-shaped curves which, it has been claimed, indicated an autocatalytic reaction. All curves round off and approach an end value asymptotically. The various data have never been taken under the same conditions and therefore must be interpreted accordingly.

Most of the work connecting combined sulfur and physical properties has been in connection with the determination of optimum cure for soft rubber. There is a general agreement in the literature that, since the acceleration varies from rubber to rubber and from compound to compound, there is no relationship between the two properties except under very specific conditions (*19*, *48*, *59*).

The tensile strength of soft rubber varies greatly with the acceleration, but that of hard rubber is independent of it.

By means of "super-accelerators" sulfur vulcanization may take place at room temperature, indicating that the process is not confined to any one temperature range (*40*, *49*). Exposure to ultra-violet light also induces sulfur vulcanization (*25*, *26*).

The Peachy process (*44*, *45*, *46*), which consists of exposing thin sheets of rubber successively to sulfur dioxide and hydrogen sulfide, vulcanizes rubber without the aid of heat.

Exposure of rubber to the action of sulfur chloride produces a vulcanizate with many of the characteristics of sulfur-cured rubber (*6*, *28*, *43*, *66*).

The vulcanization of rubber with selenium may be brought about by the use of accelerators and the product has unusual resistance to deterioration with age (*9*, *16*). When selenium is used in combination with sulfur and an accelerator, a rubber is produced with an unusually high resistance to abrasion (*10*). When it is used as a friction between plies of fabric, ply separation is delayed (*7*, *51*). The discovery that nitro compounds would vulcanize rubber is due to Ostromuislenskii (*39*, *40*), who has shown recently that carbon black and clay are excellent activators for the reaction (*41*). Fisher

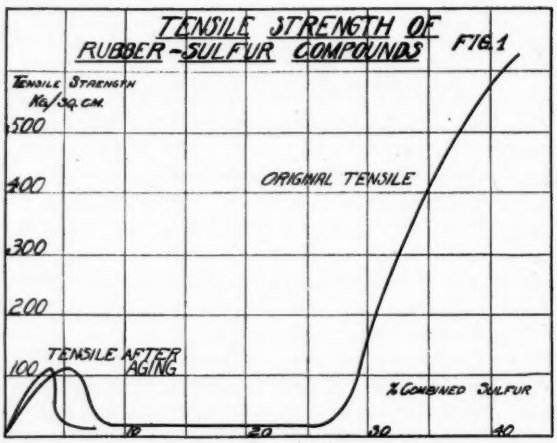
and Gray (*21*) studied the unsaturation of rubber vulcanized with these reagents and found that there is no apparent difference in this respect between vulcanized and unvulcanized rubber.

Antimony iodide has also been suggested as a vulcanizing agent (*20*).

Previous Theories of Vulcanization

The mechanical theory of vulcanization is perhaps the oldest of all. Its sponsors believed that vulcanized rubber was a sort of alloy of raw rubber and sulfur (*17*, *31*).

Ostwald's (*42*) adsorption theory was evolved in the belief that it explained the then existing data. Its chief value was in the stimulation of much experimental work to disprove entirely his ideas.



The polymerization theory postulates that vulcanization consists of the polymerization of rubber molecules under the influence of the various reagents. The fact that they react chemically with the rubber is regarded as incidental (*24*) and not essential to production of improved physical properties. The action of heat alone is regarded as a depolymerizing influence and ordinary vulcanization as the net resultant of the two effects. Twiss (*63*) has suggested that vulcanization consists of the formation of well-dispersed particles of polyprene sulfide in a matrix of raw rubber. The action of the polyprene sulfide $(C_5H_8S)_x$ is regarded as similar to that of carbon black.

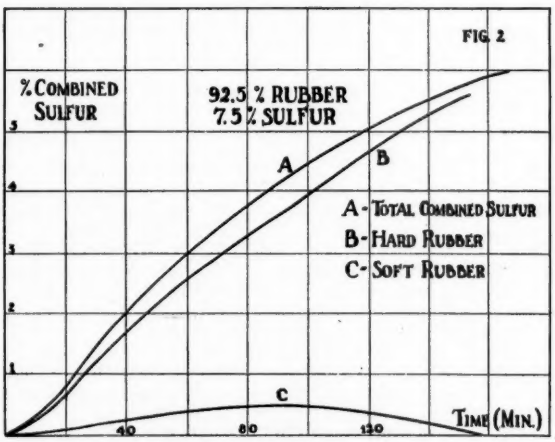
It has been suggested that the various allotropic forms of sulfur display different reactivities toward rubber and that this is responsible for some of the anomalies of vulcanization (*38*). Twiss (*62*) has shown that the rates of vulcanization do not differ from each other. This is not surprising when it is considered that it is probably only dissolved sulfur that reacts during vulcanization. It has been claimed also that

another modification of sulfur, thiozone (*4*, *19a*), is the active material. Since thiozone is apparently incapable of existing at elevated temperatures, its function in ordinary vulcanization is uncertain.

The chemical theory which has been perhaps the most successful dates from the work of Weber, who showed that sulfur reacts chemically with rubber. His results were not entirely satisfactory but better data have since been obtained. The several types of combined-sulfur curves have been explained empirically, but the explanations are not in accord with the well-established laws of chemical kinetics.

Outline of New Theory

The new theory presented here was first outlined (*10*) in connection with a study of selenium vulcanization and amplified in the discussion of another paper (*7*). The theory may be summarized in the following eleven postulates:



(1) Vulcanization of rubber is a chemical reaction in which the vulcanizing agent adds to all or a portion of the double bonds of the rubber molecule.

(2) There are two possible stable addition products of vulcanizing agents and rubber—soft vulcanized rubber and ebonite.

(3) There are two types of chemical unsaturation in the rubber molecule corresponding, respectively, to these two products. After the soft-rubber bonds are satisfied, the addition of sulfur to a portion of the double bonds concerned in hard-rubber formation gives rise to a third and unstable type of material, which we call intermediate or partially formed hard rubber.

(4) Certain vulcanizing agents undergo only the soft-rubber reaction, since they are incapable of adding to all the double bonds.

(5) The two chemical reactions occur successively in any one molecule during vulcanization with sulfur.

(6) Accelerators speed up the soft-rubber reaction but have practically no effect on the hard-rubber reaction. The maximum physical properties of soft vulcanized rubber are obtained

when the soft-rubber formation is completed with the production of a minimum amount of intermediate hard rubber.

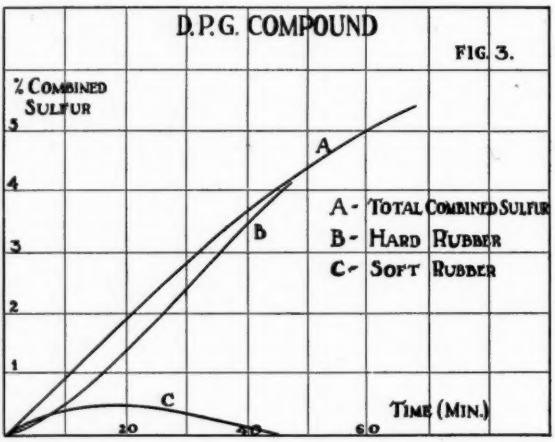
(7) There is a definite relationship between the physical properties and the combined sulfur of vulcanized rubber only when intermediate hard rubber is not formed.

(8) The amount of combined sulfur needed to produce pure soft rubber is approximately 0.5 per cent, which corresponds to $(C_5H_8)_{200}S_2$.

(9) The normal deterioration of soft rubber with age is due to the oxidation of the rubber molecule when the hard-rubber reaction has been started but not completed.

(10) During hard-rubber formation the sulfur adds progressively from one end of the molecule to the other. This gives rise to dipoles which have a maximum effect when the reaction is about half completed. This offers an adequate explanation of the electrical properties.

(11) The reclaiming of rubber results in the decomposition of the vulcanized rubber molecule into two portions, one containing practically all the combined sulfur and being insoluble in chloroform, and the other sulfur-free and soluble.



A Chemical Reaction

Vulcanization is dependent entirely on a chemical process. No vulcanized rubber has yet been produced, the writers believe, without a chemical combination of rubber with the vulcanizing agent. The combination of sulfur is well known. Vulcanization by means of ultra-violet light always results in combined sulfur. One of the writers has shown that even nitro compounds, such as dinitrobenzene and trinitrobenzene (Part II) and selenium (Part III), unite chemically with rubber. This viewpoint is contrary, of course, to the ideas of several rubber chemists (*24*).

Two Stable Products of Vulcanization

The evidence seems conclusive that the normal end product of vulcanization is ebonite. This compound is completely saturated, one sulfur atom having added to the double bond of each C_5H_8 group in the rubber molecule.

The relationship between the coefficient of vulcanization and physical properties over the whole range of combined sulfur is not a simple one, and it indicates a second possible compound of rubber and sulfur.

If the tensile strength of a rubber-sulfur mix is plotted against combined sulfur, the formation of two vulcanizates is well illustrated. (Figure 1) In the compound used (rubber 70, sulfur 30) soft vulcanized rubber has been completely formed at 5 per cent combined sulfur and has entirely disappeared at 7.5 per cent. From this point to a sulfur coefficient of nearly 30 is the region of intermediate hard rubber, which is a leather-like material characterized by an absence of tensile strength and aging ability. At 30 per cent sulfur the formation of true hard rubber begins and proceeds rapidly until a coefficient of 47.1 is reached. Glancy, Wright, and Oon (*22*) state that the physical properties characteristic of hard rubber begin to develop when one atom of sulfur has combined with one $C_{10}H_{16}$ or, in other words, when the reaction is half completed. He, however, did not plot tensile strength against combined sulfur but tensile strength and combined sulfur against time of cure. In the above curve it is quite evident that the characteristics do not start to develop until the sulfur is two-thirds combined and the hard-rubber tensile is not approached closely until combination is nearly complete. Polyprene monosulfide $(C_{10}H_{16}S)_x$, therefore, has no significance in the formation of hard rubber and if it exists at all is but an intermediate step in disulfide production.

The peak in the curve at the low value of sulfur indicates full development of soft vulcanized rubber. The only reasonable conclusion is that there is a chemical compound formed which subsequently disappears as the reaction proceeds.

Soft rubber and hard rubber are two entirely different chemical products. This is evidenced by the fact that the former is essentially an elastic material and is not affected seriously by moderate temperature changes, while hard rubber is quite susceptible and is essentially thermoplastic.

Two Types of Unsaturation in Rubber

Since all the sulfur that combines with the rubber adds to the double bonds and since it appears that there are two distinct chemical compounds capable of being formed by the reaction, there must be two types of unsaturation in the rubber molecule. One of these when combined with sulfur gives soft rubber, and when the sulfur has combined with all the double bonds hard rubber results. These types of unsaturation are of different reactivities, the more reactive being the one concerned in soft-rubber formation.

Limited Reactivity of Certain Reagents

When rubber is vulcanized with selenium or nitro compounds, only soft rubber is formed. The writers have never been able to obtain a product even remotely resembling hard

rubber by the use of these reagents. The employment of large quantities of the vulcanizing agents, active accelerators, high temperatures, and long times of heating has failed to give an ebonite-like material. In other words, these reagents only undergo the soft-rubber reaction, contrasting with sulfur, which is a reagent for both reactions. The hard-rubber reaction is apparently the more difficult one to bring about.

The heat of vulcanization studies in Part I also confirm this part of the theory. The formation of hard rubber is a strongly exothermic reaction while soft-rubber production involves no heat interchange. The vulcanization of a rubber-sulfur mix has been studied over the entire range 0 to 47 per cent combined sulfur. From zero to about 6 per cent combined sulfur (soft-rubber range) there is no measurable heat interchange. From 6 to 47 per cent there is a steady evolution of heat approximately proportional to the increase in combined sulfur. The vulcanization of rubber with selenium and dinitrobenzene involves no heat interchange. This is additional evidence that these reagents do not undergo the hard-rubber reaction. It would seem, therefore, that soft-rubber formation with sulfur is a phenomenon of the same general type as vulcanization with selenium and the nitro compounds.

Kinetics of Vulcanization

The kinetics of sulfur vulcanization has never been satisfactorily explained on a chemical basis. Only in the case of Spence's work (*56*) has the reaction been evaluated mathematically, and his formulation probably has no chemical significance. In Part III it has been shown from data of reliable origin that hard-rubber formation follows the conventional laws of chemical kinetics and is a second-order reaction, as would be expected. It has also been shown that the soft-rubber and ebonite reactions are successive. In any one rubber molecule the hard-rubber reaction cannot start until soft-rubber formation is completed.

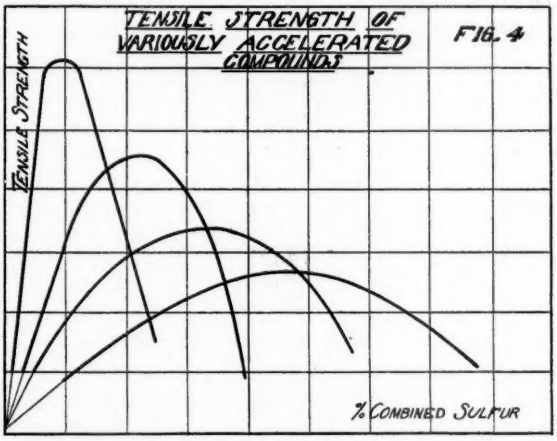
The mathematics of successive reactions is too complex to allow complete proof of this theory. In the case of hard-rubber formation, however, the soft-rubber reaction plays only a minor role. The starting material of the hard-rubber reaction is soft vulcanized rubber and in practice this is supplied rapidly. The only noticeable effect on hard-rubber formation is the S shape imparted to the curve, which may be removed by application of the proper time correction.

The study of soft-rubber formation is more complicated, but the course of the reaction may be pictured qualitatively. Each of these two successive reactions involves the production of combined sulfur, which is the only index of the progress of the chemical reaction.

The rate of the hard-rubber reaction is proportional only to the amount of sulfur present and to the concentration of the soft rubber. It is practically unaffected by accelerators. The sulfur that has combined in the formation of hard rubber

will be represented by the general type of curve, such as *B* in Figure 2. The speed of the soft-rubber reaction is proportional to both the concentration of sulfur and the raw rubber present. The amount of soft rubber present at any given time is the total quantity that has been formed minus that which has been converted into partially formed hard rubber. The soft-rubber reaction is quite sensitive to accelerating influences. The amount of sulfur in the soft rubber present is represented by curve *C*. The per cent total combined sulfur, which is the value obtained by analysis, is represented by the sum of the two curves (curve *A*).

The presence of accelerators will change somewhat the appearance of this curve *A*, depending on the relative changes produced in curves *B* and *C*. If an accelerator is present, the result will be as in Figure 3. The accelerator in this case has increased the rate of formation of soft rubber. The hard-rubber reaction rate is practically unchanged, but it has been



allowed to become important a little earlier. The fact that a straight-line relationship has been obtained by some investigators is accidental. It so happened that their curves, which represented the combined results of both the soft-rubber and hard-rubber reactions, approximated a straight line.

The vulcanization of rubber with selenium or nitro compounds provides an excellent means of studying the kinetics of soft-rubber formation, since these reagents do not undergo the complicating hard-rubber reaction. In Parts II and III it has been shown that these two reagents do react chemically with rubber and that the reactions follow the conventional first order equation.

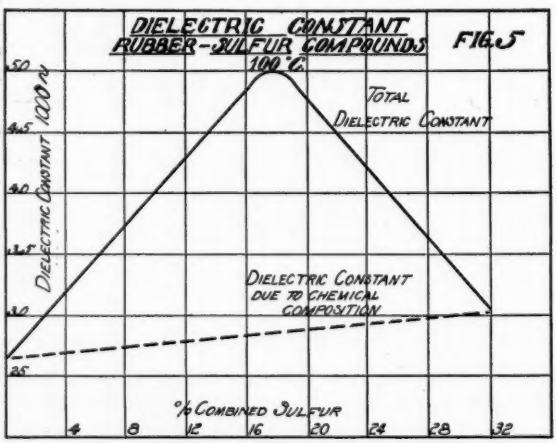
Acceleration and Combined Sulfur

The idea that the two reactions of sulfur vulcanization are successive and that accelerators affect principally the soft-rubber reaction explains the apparent anomaly of optimum

cure at various coefficients of vulcanization. As stated above, it is a general rule that the faster the acceleration the smaller is the amount of combined sulfur at optimum cure and the greater the physical properties developed.

An ordinary rubber-sulfur mix develops its optimum tensile strength at about 4 to 5 per cent combined sulfur and the product ages poorly. The addition of accelerators lowers the combined sulfur to 0.5–3.0 per cent, increases the tensile, and improves the aging. Tensile–combined sulfur curves with various degrees of acceleration would appear as in Figure 4.

Since ordinary vulcanization involves the production of both pure soft rubber and intermediate hard rubber, the physical properties of the product are determined by the relative amounts of the two constituents. Since the properties of the intermediate hard rubber are poor, the best product will be formed when its quantity is at a minimum. The more nearly the material approaches pure soft rubber the better will be the aging and the higher will be the tensile.



Accelerators affect principally the soft-rubber reaction. With no accelerator present it proceeds slowly. As soon as any one molecule of rubber has completed the soft-rubber reaction, the hard-rubber reaction starts immediately at a rate that is practically dependent only on the temperature and the concentration of the reactants. In the long time required to reach optimum cure much partially formed hard rubber with its attendant combined sulfur will be produced. The net result is high combined sulfur and low physical properties.

In the case of rapid accelerators the soft-rubber reaction is hastened, a minimum amount of intermediate hard rubber is produced, a low value of combined sulfur is obtained, and excellent physical properties are developed. It is thus obvious that the combined sulfur at an optimum cure can vary, depending on the acceleration. In any one rubber compound

where there is a definite value for the rate of cure, the amount is fixed. Optimum physical properties occur when the amount of pure soft rubber is at a maximum. The writers' experiments indicate that about 0.5 per cent combined sulfur is necessary and sufficient to produce soft vulcanized rubber. It is evident that practically all the combined sulfur at optimum cure in excess of this value has been consumed in partially formed hard-rubber production and is therefore an index of the quality of the product.

In the compound in Figure 2 the amount of intermediate hard rubber present at optimum cure corresponds to about 3.5 per cent combined sulfur. The physical properties are much lower, therefore, than those of the accelerated compound in Figure 3. In this case the combined sulfur of the intermediate hard rubber is only about 1 per cent, although that of the soft rubber is the same as before.

Disaggregation

There is also the secondary effect known as heat disaggregation, which has been used in the past to explain the improved physical properties when rapid acceleration was present. Exposure of rubber to high temperatures, either during vulcanization or otherwise, decreases the physical properties of the vulcanizate formed from it. The effect is well recognized and the value of accelerators in forming superior rubber compounds has been attributed wholly to the reduction of the amount of this effect through their use. Accelerators, however, operate chiefly, not to decrease the disaggregation, but to reduce the amount of intermediate hard rubber at optimum cure.

Molecular Weight

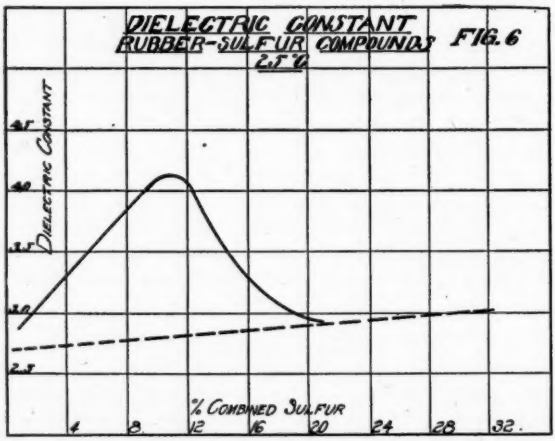
Preliminary studies on the kinetics of selenium vulcanization allow the calculation of a submultiple of the molecular weight of rubber of about 3400 or 50 isoprene molecules. The above figure of 0.5 per cent combined sulfur for soft-rubber formation, if it is assumed that at least 2 sulfur atoms react with 1 rubber molecule, gives a minimum value of approximately four times this. The rubber molecule would thus consist of 200 isoprene units.

Aging of Vulcanized Rubber

The aging curve plotted in connection with the combined-sulfur curve is very interesting. (Figure 1) Soft-vulcanized rubber ages well if the combined sulfur is kept below the value required for maximum tensile strength. As the combined sulfur is increased beyond this point, aging ability decreases rapidly, and not until hard-rubber formation is nearly complete does the rubber again age well. The rubber in this poorly aging range is a leathery material which would find commercial application if the properties could be maintained for a reasonable period of time. The writers have always

failed to produce a material of this type that ages well and apparently no one else has produced such a compound. The poor aging of these compounds is due, of course, to a strong susceptibility to oxidation. Pure soft rubber and pure ebonite resist oxidation perfectly.

As has been shown, the production of pure soft rubber with sulfur is only approached in practice since there is formed a varying amount of intermediate hard rubber. It is the presence of this material of poor aging ability that is responsible for the susceptibility of the ordinary rubber compound to oxidation. The starting of the hard-rubber reaction activates the remaining double bonds and renders them capable of adding oxygen with the attendant deterioration of the rubber. The greater the extent to which this second reaction has taken place, the faster the aging will progress. Undercured soft rubber usually ages well, since the hard-rubber reaction has been started only to a very slight extent or not at all.



Pure soft rubber would need no antioxidant to prevent deterioration. In practice it has been impossible to eliminate the formation of intermediate hard rubber but by means of super-accelerators the amount formed may be reduced to a minimum by curing at a low temperature for a short time. Such rubber ages exceptionally well.

The function of an antioxidant is to prevent the deterioration of intermediate hard rubber and its use in connection with super-accelerators allows the production of soft rubber with perfect aging properties.

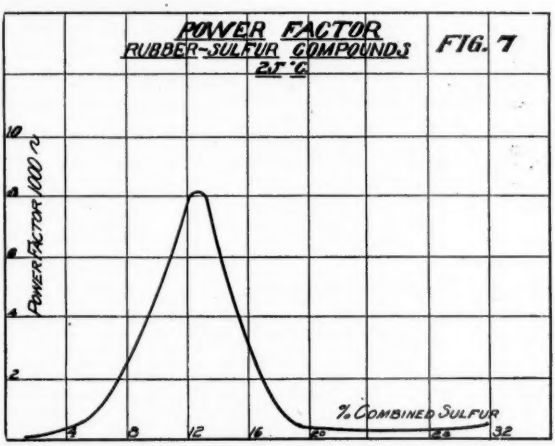
Rubber vulcanized with selenium and nitro compounds ages well, since only the soft-rubber reaction takes place. These reagents are incapable of starting the hard-rubber reaction, which would make the rubber susceptible to oxidation.

In the writers' laboratory there are samples of rubber cured thirteen years ago with selenium that are still 90 per cent as

good physically as when freshly vulcanized. Since the material was nearly pure soft rubber, no antioxidant was used and none was needed.

Chemical Structure of Rubber

The best chemical evidence today indicates that the rubber molecule is a straight-chain hydrocarbon. It is probably composed of isoprene molecules joined together through their end carbon atoms with the loss of a double bond for each union. In the final product there will be $n + 1$ double bonds per molecule, where n equals the number of isoprene units. If the value of n is large, as is ordinarily supposed, the difference between n double bonds and $n + 1$ double bonds can not be detected by analysis.

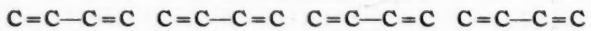


In space the chain may be in the form of a spiral, as suggested by Barrows (*2*). The double bonds in the molecule are undoubtedly separated along the chain by four carbon atoms, and in such an arrangement they would occupy nearly adjacent positions in successive loops. They would all be equivalent to each other, since each would have the same environment. Obviously, the double bonds at each end of the chain would be different in reactivity from the rest. This difference accounts for the existence of the two types of unsaturation previously mentioned. The end double bonds are the more reactive ones and probably those concerned in the formation of soft rubber. The internal double bonds, besides being less reactive owing to their position in the chain, may be so situated in the spiral that the unsaturation of adjacent pairs is mutually satisfied. This would render them unreactive except to vigorous reagents such as sulfur, halogens, and halogen acids, which react with all the double bonds. Selenium and nitro compounds apparently react only with the end double bonds to form soft rubber.

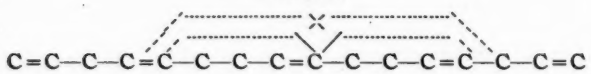
The fact that the hard-rubber double bonds tend to saturate each other explains the chemistry of aging. If the hard-rubber reaction has been well started by over-vulcanization, this condition of mutual saturation is destroyed and the remaining double bonds are activated and made susceptible to oxidation.

The following diagrams indicate this conception very roughly:

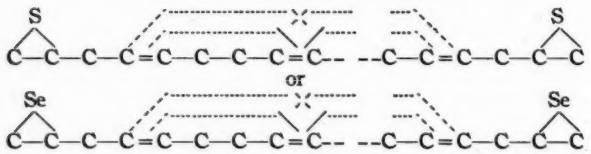
ISOPRENE MOLECULES



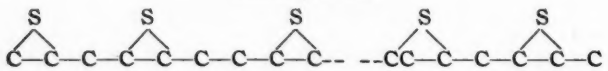
RUBBER



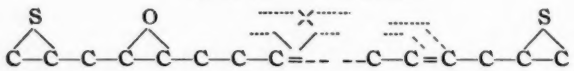
SOFT VULCANIZED RUBBER



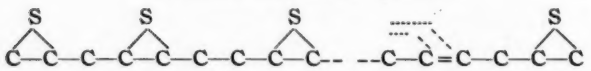
HARD RUBBER



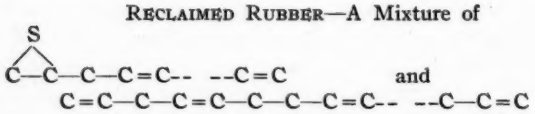
OXIDIZED SOFT RUBBER



INTERMEDIATE HARD RUBBER



RECLAIMED RUBBER—A Mixture of



Electrical Properties

The electrical properties of some viscous dielectrics were first explained in the writers' laboratory (*34*) by the Debye dipole theory and applied to rubber.

Briefly, the dipole theory postulates that many molecules, being electrically unsymmetrical, tend to orient in an electric field. In an alternating field they tend to follow the periodic changes by orienting first in one direction and then in the other. The viscosity of the medium opposes this response. When the viscosity is low the frictional resistance thus offered

is slight; as it increases the response gradually falls off, becoming negligible when the medium is solid. As the frequency of the field applied to a medium of appreciable viscosity is increased, a region is reached beyond which the molecules lose their ability to respond. This characteristic frequency obviously varies with the individual molecule and the viscosity, elasticity, or rigidity of the medium.

There are two commonly measured electrical properties of a dielectric subjected to an alternating field—dielectric constant or specific inductive capacity, and power factor. Two main components contribute to the value of the dielectric constant, the chemical composition of the material, and the effective dipolar moment of the molecules. The dipolar moment is a measure of the lack of electrical symmetry, which in turn is related to the chemical structure. The effectiveness of the dipole moment in contributing to the dielectric constant is controlled by the viscosity of the medium.

The power factor of certain types of dielectrics is used chiefly by the presence of dipoles. The power factor is a measure of the tendency of a dielectric to dissipate electrical energy. In dipolar materials it may be attributed to the frictional loss due to the rotation of the molecules in a viscous medium. This loss, therefore, would be dependent on the dipole moment, the applied frequency, and the viscosity. As the latter is increased the power factor at first rises, owing to the greater resistance offered to the turning of the dipoles. As the viscosity is increased further the power factor falls and becomes low when viscosity is extremely high, since the dipoles are then unable to follow the field. The simplest method of altering the viscosity of a medium without changing its composition is to change its temperature. Many materials show the above effects over a range of temperature that includes transition from the solid to the liquid state.

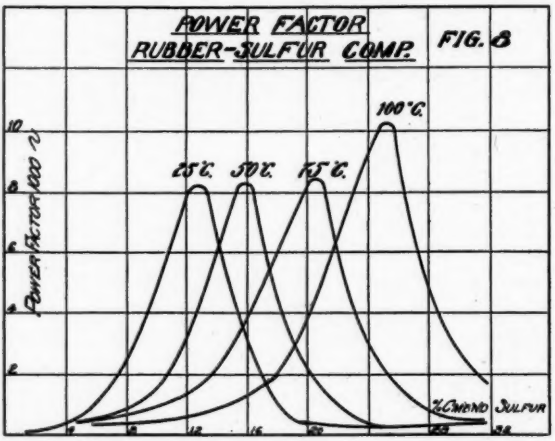
It is possible by inspecting the structural formula of a molecule to predict how changes in it will alter the dipole moment. Any change which makes the molecule less symmetrical chemically tends to increase the dipole moment. Such a change will be reflected in the dielectric constant and power factor.

The writers believe that soft-rubber formation consists in the addition of sulfur or some other reagent to the end double bonds of the molecule. Of the remaining double bonds which are concerned in hard-rubber formation, those near the end of the molecule would be the most reactive and the first to combine with sulfur. The first addition of sulfur activates the adjacent double bonds. Addition of sulfur to these in turn activates the next ones. The combination with sulfur thus proceeds progressively from one end of the molecule to the other. The molecules of crude rubber, soft-vulcanized rubber, and ebonite are symmetrical and non-dipolar. The dielectric constants of these materials depend, therefore, only on the empirical composition and the power factors are very low. The dielectric constant of ebonite is greater than that of raw

rubber owing to the change from $(C_5H_8)_x$ to $(C_5H_8S)_x$. As hard-rubber formation proceeds the dissymmetry increases until half of the double bonds have combined with sulfur. Combination beyond this point increases the symmetry until hard rubber is completely formed and the molecule again balanced.

Neglecting the change in viscosity of rubber with per cent combined sulfur, we should expect the dielectric constant to rise as the addition of sulfur takes place, reach a maximum at a coefficient of 23, and decrease again as the hard-rubber formation is completed. Under certain chosen conditions this is found to be so (Figure 5), thus confirming the general theory of the course of vulcanization.

The electrical behavior of vulcanized rubber is complicated by the fact that the addition of sulfur not only alters the dipole moments of the individual molecules, but also simultaneously changes the physical characteristics of their environment.



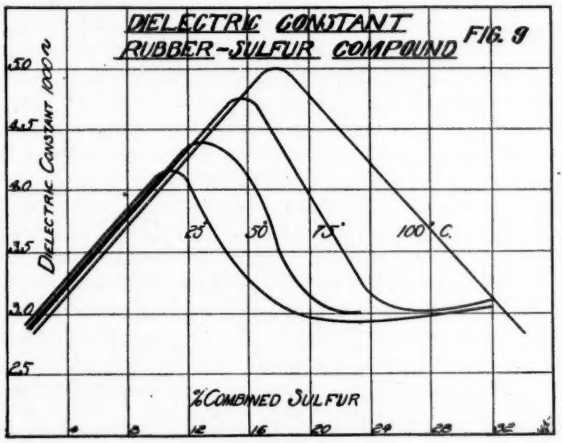
Thus with low combined sulfur the material is soft and elastic, while as it is increased the rubber becomes hard and rigid. This change in rigidity has the same effect in rubber as altering the viscosity of a liquid. This behavior is illustrated by the curve of dielectric constant *vs.* combined sulfur of a rubber-sulfur mix at room temperature. At a definite value for combined sulfur the dielectric constant, which had been steadily rising, drops sharply to the value corresponding to the empirical chemical formula. (Figure 6) The power factor which is initially low, rises with increase in rigidity to a maximum and then falls again to a low value, as the rigidity of the medium prevents the dipoles from responding to the field. (Figure 7) These curves are entirely changed, of course, by a variation of temperature which, although it does not alter the electrical moment of the dipoles at any one sulfur content, affects their response by altering the rigidity of the rubber. (Figures 8 and 9) The power factor curve at 100° C.

indicates that the viscosity effect has been practically eliminated at this temperature. As a result the corresponding curve for dielectric constant pictures the formation of dipoles as predicted by the theory. (Figure 5)

It is not out of place, perhaps, to suggest that the orientation of rubber molecules offers a valid explanation of the Joule effect.

Note—Since the paper was presented the review of Hock's work in Memmler's "Handbuch der Kautchuk Wissenschaft," 467, Leipzig, 1930, has been called to the writers' attention. It is interesting to note that Hock has postulated independently a similar theory of the Joule effect.

The long-chain rubber molecules at ordinary temperatures are in rapid thermal motion, involving both a translatory displacement and a rotation about their individual axes. When rubber is stretched the mechanically applied tension causes at least a partial orientation of the molecules, as is evidenced by the development of double refraction and an x-ray diffraction pattern. The fibrous structure shown when chilled,



stretched rubber is shattered by an impact visually demonstrates the lining up of the molecules.

This orientation due to stretching results in a loss of kinetic energy in the individual molecules on account of the restriction of thermal motion, which instantly appears in the mass of rubber as heat. The other phases of the Joule effect are similarly explained. The retraction of stretched rubber allows the molecules again to assume their random thermal motion, and the energy absorbed in this is drawn from the surroundings by a cooling of the rubber. The application of heat to stretched rubber increases the tendency for molecular motion, which reduces orientation and shortens the rubber accordingly or increases the tension required to maintain the stretched condition.

Reclaimed Rubber

The present theory of vulcanization is capable of explaining

the process of reclaiming rubber. Vulcanized rubber is ordinarily reclaimed for re-use by being heated with either acid or alkali at high steam pressures and temperatures. The process changes the resilient and elastic raw material to a soft and plastic mass which may be milled readily into a rubber compound. Before it is reclaimed the material is almost entirely insoluble in chloroform, but after treatment about one-third of the rubber hydrocarbon has become soluble. For many years the completeness of the action has been judged by the writers by the amount of this constituent.

Ordinarily, unvulcanized rubber may be distinguished from vulcanized rubber by its solubility in chloroform. The reclaiming process would seem, therefore, to have devulcanized about half the rubber hydrocarbon. The original material has a combined sulfur content of 3 to 7 per cent. After the treatment the entire amount of sulfur will be found in the chloroform-insoluble fraction. The chloroform extract is practically sulfur-free.

In vulcanized rubber each molecule contains combined sulfur. The writers have postulated in their theory that soft-rubber formation involves the addition of sulfur to the ends of the rubber molecule. The evidence, then, indicates that the central portion of the molecule, containing no sulfur, becomes separated from the remainder during the reclamation to produce the chloroform-soluble material. This leaves the sulfur-containing end portions separate and they constitute the chloroform-insoluble portion of the reclaim. The process has thus made fresh end double bonds available for the addition of sulfur again to form a soft-vulcanized rubber. Since the process has reduced the size of the molecules, it would be expected that the physical properties of the material, when vulcanized, would be inferior to those of vulcanized raw rubber. A second reclaiming should reduce further the molecular size and correspondingly decrease the value of the material This seems to be consistent with experience.

Literature Cited

(1) Bacon, *J. Phys. Chem.*, **32**, 801 (1928).
(2) Barrows, *Armour Engineer*, **6**, 167 (1913); *C. A.*, **7**, 3547 (1913).
(3) Bayer, etc., German Patent 280,198 (1914).
(4) Bedford and Sebrell, J. IND. ENG. CHEM., **14**, 25 (1922).
(5) Bedford and Sebrell, *Ibid.*, **13**, 1034 (1921).
(6) Bernstein, *Kolloid-Z.*, **11**, 185 (1912).
(7) Blake, *Rubber Age*, **24**, 494 (1929).
(8) Boggs, U. S. Patent 1,296,469 (1919).
(9) Boggs, U. S. Patents 1,249,272 (1917); 1,364,055 (1920); J. IND. ENG. CHEM., **10**, 117 (1918).
(10) Boggs and Follansbee, *Trans. Inst. Rubber Ind.*, **2**, 273 (1926).
(11) Bolas, *J. Soc. Arts*, **28**, 763 (1880).
(12) Bourn, *J. Soc. Chem. Ind.*, **32**, 760 (1913).
(13) Bruni, U. S. Patent 1,386,153 (1921).
(14) Burke, English Patent 12,591 (1849).
(15) Cranor, *India Rubber World*, **61**, 137 (1919).
(16) Ditmar, *Gummi-Ztg.*, **19**, 576, 578 (1905); **29**, 425 (1915).
(17) Donath, *Z. Chem. Ind. Kolloide*, **1**, 77 (1877).
(18) Dubosc, *Caoutchouc & gutta-percha*, **13**, 8886 (1916).

(19) Eaton and Day, J. Soc. CHEM. IND., **36**, 1116 (1917).
(19*a*) Erdmann, *Ann.*, **362**, 133 (1908).
(20) Fawsitt, *J. Soc. Chem. Ind.*, **11**, 332 (1892).
(21) Fisher and Gray, IND. ENG. CHEM., **20**, 294 (1928).
(22) Glancy, Wright, and Qon, *Ibid.*, **18**, 73 (1926).
(23) Goodyear, U. S. Patent 3,633 (1844).
(24) Hauser, *Trans. Inst. Rubber Ind.*, **2**, 301 (1926).
(25) Heilbronner and Bernstein, *Comp. rend.*, **158**, 1343 (1914).
(26) Henri, *Caoutchouc & gutta-percha*, **7**, 4371 (1910).
(27) Heurn, van, Comm. Dutch Rubber Inst., Vol. VII, p. 242.
(28) Hinrichsen and Kindscher, *Kolloid-Z.*, **6**, 202 (1910).
(29) Hinrichsen and Kindscher, *Ber.*, **26**, 1291 (1913); *Kolloid-Z.*, **11**, 191 (1912).
(30) Hohn, *Gummi-Ztg.*, **14**, 17, 34 (1899).
(31) Hohn, *J. Soc. Chem. Ind.*, **18**, 1034 (1899).
(32) Immisch, U. S. Patent 937,745 (1909).
(33) Iterson, van, Comm. Dutch Rubber Inst., Vol. VII, p. 239.
(34) Kitchin, *Trans. Am. Inst. Elec. Eng.*, **48**, 495 (1929).
(35) Luff and Porritt, *J. Soc. Chem. Ind.*, **40**, 275T (1921).
(36) Moureau and Dufraisse, *Bull. soc. chim.*, **31**, 1152 (1922).
(37) Murrill, U. S. Patents 1,622,534; 1,622,535; 1,622,536 (1927).
(38) Nordlander, Paper presented before the Rubber Division at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.
(39) Ostromuislenskii, *J. Soc. Chem. Ind.*, **35**, 59, 369 (1916).
(40) Ostromuislenskii, U. S. Patent 1,342,457 (1920).
(41) Ostromuislenskii, U. S. Patent 1,696,409 (1928); *India Rubber World*, **80**, No. 3, 55 (1929).
(42) Ostwald, *Kolloid-Z.*, **6**, 136 (1910); **7**, 45 (1910).
(43) Parks, English Patent 11,147 (1846).
(44) Peachy, English Patent 129,826 (1919).
(45) Peachy, *India Rubber J.*, **59**, 1195 (1920).
(46) Peachy, English Patent 162,429 (1921).
(47) Pummerer and Burkhard, *Ber.*, **55**, 3458 (1922).
(48) Schidrowitz and Gouldsboro, *India Rubber J.*, **51**, 505 (1916); **53**, 327 (1917).
(49) Scott and Bedford, J. IND. ENG. CHEM., **13**, 125 (1921).
(50) Skellon, *Kolloid-Z.*, **14**, 96 (1914).
(51) Somerville and Cope, *T. Inst. Rubber Ind.*, **4**, 263 (1928).
(52) Spence, *Kolloid-Z.*, **9**, 300 (1911).
(53) Spence and Scott, *Ibid.*, **8**, 304 (1911).
(54) Spence and Ward, *Ibid.*, **11**, 274 (1913).
(55) Spence and Young, *Ibid.*, **11**, 28 (1912).
(56) Spence and Young, *Ibid.*, **13**, 265 (1913).
(57) Spiller, *J. Chem. Soc.*, **18**, 44 (1865).
(58) Stevens, *Rubber Age (London)*, **4**, 194 (1923).
(59) Stevens, *India Rubber J.*, **53**, 220, 366 (1917).
(60) Stevens and Stevens, *J. Soc. Chem. Ind.*, **48**, 557 (1929).
(61) Twiss, *Ibid.*, **36**, 782 (1917).
(62) Twiss, *Ibid.*, **40**, 48T (1921); Annual Reports of Applied Chemistry, Vol. IV, p. 327 (1919).
(63) Twiss, *J. Soc. Chem. Ind.*, **44**, 106T (1925).
(64) Weber, "Chemistry of India Rubber," p. 86.
(65) Weber, *Ibid.*, p. 91.
(66) Weber, *J. Soc. Chem. Ind.*, **13**, 14 (1894).
(67) Whitby and Jane, *Trans. Roy. Soc. Can.*, III, **20**, 121 (1926); *Ber.*, **59**, 682 (1926); *India Rubber J.*, **72**, 295 (1926).
(68) Williams, U. S. Patent 1,685,386 (1928).

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Solubility of Oxygen in Rubber and Its Effect on Rate of Oxidation[1]

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A study has been made of the effect of the concentration of oxygen in rubber upon its aging properties. Such factors as temperature and pressure on the solubility of oxygen in rubber have been studied.

The solubility of oxygen in rubber follows Henry's law and decreases with increasing temperature. The oxidation of rubber proceeds at a uniform rate as long as the oxygen concentration remains above a certain minimum. The concentration of oxygen in rubber exposed to air at 70° C. is less than that required to produce uniform oxidation at a maximum rate. High temperature appears to produce a type of oxidation which is affected by high pressure. The simultaneous use of high temperature and high pressure should be avoided.

ONE of the important tests applied to rubber is intended to determine its probable deterioration with age. It has long been recognized that the deterioration is caused principally by oxidation and two tests have been devised for increasing the speed of oxidation. The Geer test increases the rate of the reaction by placing the rubber in air at an elevated temperature. The Bierer-Davis test employs both an elevated temperature and an atmosphere of oxygen under pressure. It is well known that at elevated temperature the rubber is affected by factors other than oxidation, such as continuation of vulcanization, volatilization of materials from the rubber, and solubility of various ingredients contained in the rubber. No consideration seems to have been

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given to the effect of change in the concentration of oxygen under various conditions of testing.

The concentration of oxygen would be expected to affect the rate of oxidation of rubber. This supposition would seem to be justified by the fact that rubber deteriorates more rapidly at 70° C. if the oxygen pressure is increased. If the concentration of the rubber remains constant, so that the oxidation reaction could be considered to revert to a type as simple as the first order, the increase in oxygen pressure from that of atmospheric oxygen to 21.1 kg. per sq. cm. (300 lbs. per sq. in.) will increase the deterioration rate 100 times, or $3^1/_2$ days in the bomb would equal 1 year of aging in the oven. This condition is not found in practice. If the oxidation reaction is of a higher order, the increase in pressure should make the rate in the bomb at 70° C. extremely rapid. This emphasizes the importance of the knowledge of the concentration of oxygen under different conditions.

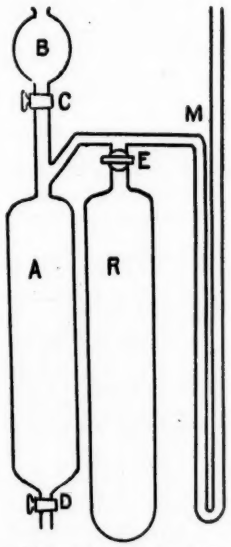

Figure 1—Apparatus for Measuring Solubility of Oxygen

Most of the previous work on the solubility of gases in rubber has been related to their permeability through rubber. Venable and Fuwa (*6*) investigated the effect of pressure and temperature on the solubility of carbon dioxide in rubber and correlated the data so obtained with the permeability of this gas. They also found values for the solubility of various other gases at one temperature and pressure. No detailed study of the effect of temperature and pressure on the solubility of oxygen in rubber was made.

Venable and Fuwa showed that the solubility of a gas is the same for both crude and vulcanized rubber. For this reason the present study of solubility was not extended to determine the effect of cure.

The sample used was composed of smoked sheet 100, zinc oxide 1, sulfur 2, and tetra-methylthiuram monosulfide 0.25 parts. The cure was 15 minutes at 125° C. This gave a stock which was free from porosity and was lightly enough compounded to be essentially pure rubber.

The source of oxygen was a cylinder of the compressed gas which was not further purified before use in the determination.

The apparatus used in carrying out the determination is shown in Figure 1. Before assembling the apparatus the bulb *R* was filled with a known weight of the vulcanized rubber cut into strips 150 × 2 × 2 mm. The stopcock *E* was then sealed to the bulb and the free gas space inside the bulb

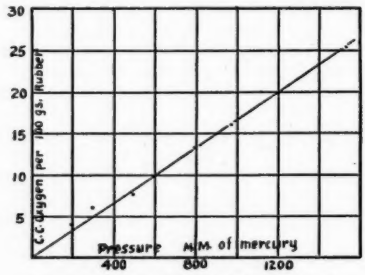

Figure 2—Change of Solubility of Oxygen with Pressure

determined. To make this determination the tube was first evacuated, weighed against a glass counterpoise of the same size, and then filled at room temperature with freshly boiled distilled water and reweighed. From these weights and the density of water at the temperature of the determination the free volume in the bulb was then calculated and found to be 79.4 cc. The water was then removed from the tube and the tube dried by continued evacuation at an elevated temperature. The volume of tube *A* was approximately 100 cc. The manometer *M* was long enough to permit measurement of pressures in the system from a few millimeters to 2 atmospheres. *B* is an ordinary dropping funnel which was sealed to the system.

When carrying out a determination the funnel *B* was filled with mercury and the system evacuated through stopcock *D*. The stopcock *E* was then closed and oxygen was run in through stopcock *D* until the desired pressure was obtained, after which *D* was closed. The bulbs *A* and *R* were then surrounded by a constant-temperature bath. When a temperature equilibrium was reached the position

of the mercury in the manometer was recorded. Stopcock *E* was then opened to admit the oxygen to the rubber. Mercury was then added from *B* until the level of mercury in the manometer was back to its original position. As more oxygen dissolved more mercury was added from *B*.

At room temperature $1^1/_2$ hours were required for equilibrium. At lower temperatures the time was increased, the time allowed at 0° C. being 24 hours. After equilibrium had been reached the mercury was removed and weighed. From the density of mercury at the temperature of the determination the volume of mercury was computed. This gave the volume of gas in the bulb *R* and the free gas space in tube *R* being known, the amount of gas dissolved under the conditions of the experiment was given by difference.

In reporting the values of the solubility of oxygen in rubber the results have all been calculated in terms of cubic centimeters of gas at 0° C. and 760 mm. pressure per 100 grams of rubber. At other than room temperature the correction in the free gas space of bulb *R* due to the difference in coefficient of expansion of the rubber and the glass has been applied.

Effect of Pressure

In determining the effect of pressure on the solubility of oxygen in rubber the constant temperature of 29° C. was arbitrarily chosen. The solubility of oxygen was measured at pressures from 193 to 1538 mm. of mercury. The results of these determinations are given in Table I and Figure 2.

Table I—Effect of Pressure on Solubility of Oxygen in Rubber

Pressure	Oxygen Dissolved in Rubber
Mm.	*Cc./100 grams*
193.4	4.00
296.4	6.05
493.4	7.68
795.2	13.40
972.2	16.05
1538.0	25.40

It will be seen from the graph that the solubility of oxygen in rubber follows Henry's law—i. e., the quantity of a gas taken up by a given volume of solvent is proportional to the pressure of the gas. At atmospheric pressures the addition of 0.1 cc. of mercury produced a noticeable effect in the level of the manometer. At lower pressures the apparatus was not so sensitive, which explains why the two lowest points are slightly out of line.

Effect of Temperature

The study of the effect of temperature was carried out at 760 mm. pressure. Temperatures from 0° to 100° C. were investigated. At higher temperatures a much higher solubility was found than was expected, and was due to oxidation during the experiment. In order to get more accurate determinations at the higher temperatures, a small amount of hydroquinone

was introduced into tube R through stopcock E, the tube was then well evacuated and warmed up to cause the hydroquinone to diffuse into the rubber. Measurements of the

Table II—Effect of Temperature on Solubility of Oxygen in Rubber

Temperature	Oxygen Dissolved in Rubber
° C.	*Cc./100 grams*
0	25.62
12	18.58
29	12.50
45	12.25
60	14.90
100	35.40
PROTECTED WITH HYDROQUINONE	
60	13.10
100	21.65

solubility made after the protection of the stock by the hydroquinone show more normal values, but even with this protection oxidation took place and no equilibrium was reached. The results of these experiments are given in Table II and Figure 3.

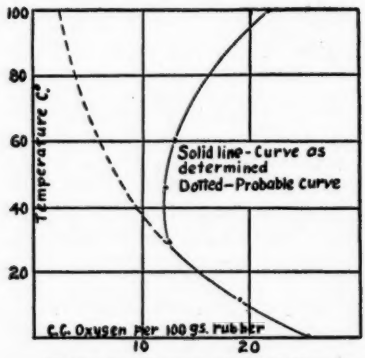

Figure 3—Change of Solubility of Oxygen with Temperature

These data show that the solubility decreases with increasing temperature. In plotting the solubility curve the values at 60° and 100° C. are those obtained with protected rubber. This portion of the curve has, however, no significance, since an equilibrium condition was never reached, and the figures are a measure of combined solubility and oxidation. The dotted portion of the curve gives the probable course of the solubility if not influenced by oxidation. This curve was drawn after consideration had been given to the curve obtained by Venable and Fuwa (*6*) for the solubility of carbon dioxide.

It is interesting to note that Morris and Street (*4*) report difficulty in measuring the permeability of air through rubber at high temperature. This trouble may have been due to a removal of part of the oxygen of the air by oxidation as it passed through the rubber membrane.

Rate of Absorption of Oxygen by Rubber

In order to obtain more information in regard to the

mechanism of oxidation, absorption experiments were devised similar to those reported by Kohman (*2*) and Marzetti (*3*). Glass bulbs having a capacity of about 14 cc. were sealed to the end of a heavy capillary tube 84 cm. in length. A small opening in the bulb opposite the capillary tube was closed with a glass stopper. The capillary tube was led through the bottom of a water bath by means of a connection similar to that used on an ordinary Liebig condenser, so that the bulb could be immersed and maintained at any desired temperature. The rubber to be tested was ground on a mill until it was in the form of small particles or a thin sheet. If unvulcanized rubber was tested, thin pale crepe was used. Two grams of rubber were placed in the bulb, which was then flushed out with oxygen and closed. The end of the capillary was placed in a reservoir of mercury and the rise of the mercury column was observed at definite time intervals. Corrections were made for changes in baro-

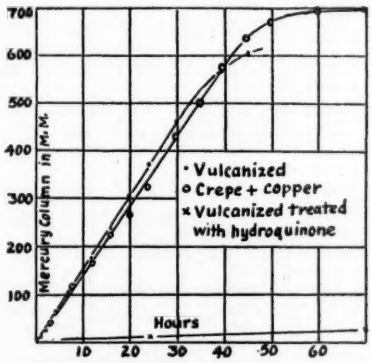

Figure 4—Absorption of Oxygen by Rubber

metric pressure during the test. If the bulb was closed at 0° C., the amount of oxygen which is available is 1 per cent of the weight of the rubber. Marzetti (*3*) has shown that this amount of oxygen is sufficient to destroy the physical properties of the rubber.

The curves obtained resemble those obtained by plotting combined sulfur against time of cure. The combination proceeds at a uniform rate until most of the oxygen is consumed, after which the rate slowly decreases until the maximum amount of oxygen has been used. The amount of pressure remaining in the bulbs at the end of the test varies somewhat from one sample to another, but is generally not more than 5 or 6 cm. of mercury when tested at room temperature.

A sample composed of 100 parts of smoked sheet rubber and 10 parts of sulfur was vulcanized for 5 hours at 140° C. and, after grinding on the rubber mill, was acetone-extracted and dried. Two-gram samples were then placed in each of

two bulbs and tested at 25° C. In one bulb a small amount of solid sodium hydroxide was introduced. After absorption of oxygen was complete, the residual pressure in the bulb containing no caustic was 54 mm. of mercury while the pressure in the bulb containing caustic was reduced to 30 mm. of mercury. The small decrease in pressure caused by the presence of caustic indicated that at 25° C. not more than traces of water and carbon dioxide are formed. The final pressure remaining in the bulbs is largely due to gases such as nitrogen which are dissolved in the rubber and to impurities in the oxygen employed.

Three samples were prepared for testing as follows:

(1) A mixture of 100 parts of smoked sheet rubber and 10 parts of sulfur was vulcanized for 5 hours at 140° C. after which it was ground on the mill, acetone-extracted, and dried in the air. It was exposed to the air for 24 hours in order to avoid any induction period in the oxidation such as has been suggested by Ostwald (*5*) and others. This exposure is standard in all tests unless otherwise stated.

(2) The above sample, after acetone extraction, was immersed in a saturated solution of hydroquinone in acetone for 2 hours, after which it was quickly rinsed with a small amount of acetone and dried.

(3) Acetone-extracted pale crepe was immersed in a saturated solution of cupric stearate for several days, after which it was dried in air.

The oxygen-absorption tests were carried out at 27° C.

The results obtained with these three samples are given in Table III and are plotted in Figure 4.

Table III—Rate of Combination of Oxygen with Rubber at 27° C.

Time	Height of Hg Column			Time	Height of Hg Column		
	Sample 1	Sample 2	Sample 3		Sample 1	Sample 2	Sample 3
Hours	*Mm.*	*Mm.*	*Mm.*	*Hours*	*Mm.*	*Mm.*	*Mm.*
1	11	...	12	30	461	...	430
2	24	...	28	35	...	...	501
3	...	...	40	40	...	...	572
4	67	...	...	45	604	...	635
8	114	...	111	50	...	...	673
12	175	...	164	60	...	...	695
16	237	...	220	70	...	23	700
20	305	...	268	141	...	33	
24	372	11	322	1245	...	140	

These results show the oxidation of both the unvulcanized rubber in the presence of copper and of the vulcanized rubber to be independent of the oxygen concentration as long as the oxygen concentration is maintained above a certain minimum. This indicates a series of reactions and the figures obtained are an indirect measure of the slowest reaction which precedes the oxidation, and not of the faster reaction which is responsible for the absorption of oxygen. While no information in regard to the nature of any other action is gained, it is clear that, since oxygen absorption takes place at a constant rate, the concentration of the reacting material remains practically constant. Since rubber is the only material present in large amounts, the most plausible explanation lies in some reaction involving only rubber which slowly

produces a type capable of being oxidized. This reaction may be reversible, since no conditions have been found for treating the rubber to build up a high concentration of the active type and produce an initial very rapid rate of oxidation.

The oxidation of the rubber appears to be an addition reaction. If carbon dioxide or monoxide and water were formed, they would serve to produce pressure or prevent a reduction in pressure in the bulb as the oxygen is consumed. This would be especially true at higher temperatures, which would tend to keep the water in the vapor state. While both water and carbon dioxide have been reported (*2*) as appearing when the oxidation is carried out at 70° C. or above, measurements with the present type of apparatus at

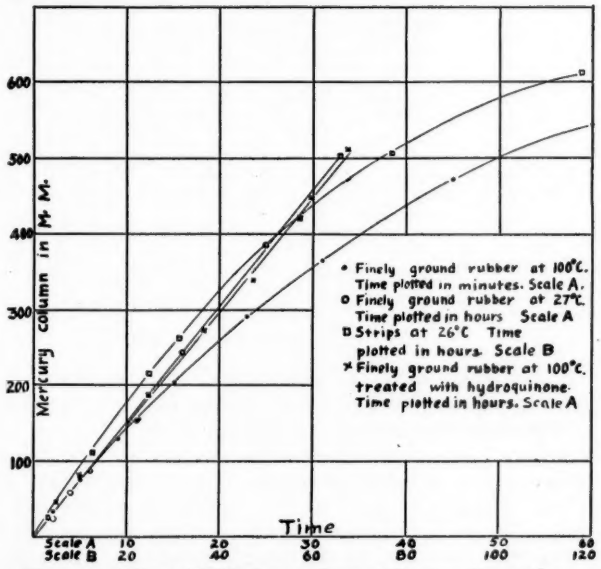
600
500
400
300
200
100
Mercury column in M. M.
• Finely ground rubber at 100°C. Time plotted in minutes. Scale A.
o Finely ground rubber at 27°C. Time plotted in hours Scale A
□ Strips at 26°C Time plotted in hours. Scale B
× Finely ground rubber at 100°C. treated with hydroquinone. Time plotted in hours. Scale A
Time
Scale A 10 20 30 40 50 60
Scale B 20 40 60 80 100 120

Figure 5—Effect of Diffusion on Rate of Oxygen Absorption

elevated temperatures show that the quantity must be quite small when the oxygen pressure is atmospheric or less.

Temperature Coefficient of Oxidation

The temperature coefficient of oxidation was determined for both the acetone-extracted crepe after treatment with copper and for the extracted vulcanized rubber. The rate was determined on the same sample without opening the bulb or introducing fresh oxygen. This was done by running the test only long enough at each temperature to establish definitely the slope of the curve showing absorption of oxygen against time. Each increase in temperature caused an expansion of the oxygen and partly overcame the decrease in pressure caused by the previous absorption. For this reason the series of tests can be conducted without decreasing

the pressure in the bulb to less than half the original. After each temperature change readings were taken until the rate of absorption of oxygen became constant. Determinations were made on two samples of each rubber. (Table IV)

Table IV—Temperature Coefficient of Oxidation

Temp.	Vulcanized Rubber		Rubber after Cu Treatment	
	Sample 1	Sample 2	Sample 1	Sample 2
° C.				
0	...	...	1	...
26	26	...	...	...
27	...	15	...	...
28	...	...	...	6.5
42	75	...	...	...
53	...	...	186	88
56	138	...	...	...
70	280	210	...	164
80	428	...	...	...
90	604	...	...	...
100	750	775	...	330

The rate of oxygen absorption is shown to double for each 7° to 10° C. rise in temperature when only the lower temperatures are considered. This temperature coefficient would indicate that the change upon which oxygen absorption is dependent is a chemical one. At higher temperatures the coefficient appears to be very much reduced. The reduction is only apparent, however, and is caused by combination of the oxygen at a rate faster than the diffusion of oxygen into the rubber which results in a low concentration inside the rubber. This is shown by the following experiments.

Effect of Diffusion of Oxygen

It was found that oxygen-absorption curves obtained at high temperatures no longer proceeded at a uniform rate, but decreased as the concentration of oxygen in the bulb decreased. Since the diffusion of oxygen into the rubber depends on the oxygen pressure, it was thought that the deviation from a straight line was caused by a deficiency of oxygen inside the rubber. If this assumption is correct, deviation from a straight line should occur at a lower temperature when larger pieces of rubber are used since the oxygen must diffuse farther. A straight line should also be obtained at a high temperature if the rate of oxidation can be made slow enough by the addition of a suitable antioxidant. Experiments were run with finely ground rubber at low and high temperatures, finely ground rubber at high temperatures after treatment with hydroquinone, and strips of rubber 4 mm. square at low temperature.

The results are shown in Figure 5. Since these curves are presented only to show their direction, the time is plotted to different scales in order to group the curves for better comparison. These curves show the dependence of uniform oxidation on both the rate of oxidation and the distance which the oxygen must penetrate. The deviation from a straight line indicates that as the pressure decreases an increasing proportion of the rubber is oxidizing at less than the maximum rate. While finely ground rubber at 100° C. does

not produce a straight line, it can be made to do so by reducing the rate of oxidation either through the addition of an antioxidant or by reducing the temperature. The more bulky rubber uses the oxygen before it can diffuse to the inside in sufficient concentration to cause uniform oxidation and a deviation from a straight line results.

Oxidation under Pressure

The oxygen bomb has become one of the standard methods of testing the age-resisting properties of rubber. Commonly accepted conditions are 70° C. and 21.1 kg. per sq. cm. (300 lbs. per sq. in.) oxygen pressure. It is well known that under these conditions the physical properties of rubber will deteriorate from three to four times as fast as the same rubber in air at normal pressure and the same temperature. This increase in rate of deterioration is not at all in proportion to the increase in oxygen pressure. If the temperature is reduced to 50° C., the influence of pressure has been shown by Bierer and Davis (*1*) to be less than at 70° C. The following tests carried out on a compound composed of 100 parts of rubber and 10 parts of sulfur which was vulcanized for 240 minutes at 140° C. confirm the findings of Bierer and Davis. This compound was aged in the oxygen bomb at a temperature of 50° C. and under pressures of 4.2, 12.65, and 21.1 kg. per sq. cm. The data in Table V show that the rate of decrease in tensile strength is not proportional to the oxygen pressure.

Table V—Effects of Oxygen Pressure on Bomb Aging at 50° C.

Time in Bomb	Tensile at Oxygen Pressure of:		
	4.2 kg./sq. cm.	12.65 kg./sq. cm.	21.1 kg./sq. cm.
Days	*Kg./sq. cm.*	*Kg./sq. cm.*	*Kg./sq. cm.*
0	193.3	193.3	193.3
1	163.5	172.2	144.1
3	137.1	124.8	79.1
5	24.6	15.8	12.5

While evidence is somewhat indefinite, the deterioration of rubber at temperatures near or above 70° C. seems to be hastened by a second type of oxidation. For instance, the oxidation is influenced by the concentration of oxygen at high temperature and becomes very violent if the pressure and temperature are increased enough. It is well known that the introduction of thin pieces of rubber into the oxygen bomb at 70° C. and 21.1 kg. per sq. cm. pressure is attended by the risk of combustion. While the tendency for this type of oxidation may be present under natural aging conditions, it becomes important only at higher temperature. If the reaction rate doubles for each 10° C. rise in temperature, a rise from 30° to 70° C. will increase the rate 16 times. If the reaction was initially slow enough this increase might not be of great importance. If the reaction is of the first order an increase in oxygen pressure from that found in air to 21.1 kg. per sq. cm. will still further increase the rate to 1600 times. It is probable that this reaction is of a still higher order, under which conditions a reaction proceeding at

a negligible rate in air at ordinary temperature will assume enormous proportions with high pressure and temperature. This is certainly the case when the rubber approaches the kindling temperature.

High oxygen pressure even at lower temperatures can have an important effect on the oxidation of various materials which may have been added to the rubber. It is known that many organic materials, especially some accelerators and antioxidants, are easily oxidized. Since these oxidation reactions are of the first or higher order, the rate is greatly increased by increase in oxygen pressure, while the rate of oxidation of the rubber remains almost unchanged. Under such conditions an antioxidant which is quite effective for natural aging would be rapidly destroyed and appear worthless.

Conclusions

It is apparent that an artificial aging test must consider the concentration of oxygen existing in the rubber. The concentration of oxygen in rubber suspended in air at 70° C. will be less than that required for normal oxidation at the maximum rate. This should limit the use of an air atmosphere to the highest quality of rubber in which the rate of oxidation is extremely small in comparison with the rate of diffusion of oxygen, and in this case tests should be confined to thin slabs.

The solubility of oxygen in rubber suspended in oxygen at 70° C. and atmospheric pressure appears to be slightly greater than that required for uniform oxidation. Under these conditions thin slabs of good or medium-quality rubber should oxidize in a satisfactory manner. The fact that strips 4 mm. square of a rubber extremely sensitive to oxidation, when tested in an oxygen atmosphere at 26° C., produce deviation from a straight line would make doubtful the accuracy of tests conducted on easily oxidized rubber under these conditions. This type of rubber would require 2 or 3 atmospheres pressure in order to maintain the required oxygen concentration. The type of deterioration appearing at higher temperatures should have little influence unless high oxygen pressure is used. The use of both high temperature and high pressure may emphasize types of oxidation which are suppressed at ordinary temperature. Since little is known about this type of oxidation, it is believed that the simultaneous use of high temperature and high pressure should be avoided.

Literature Cited

(1) Bierer and Davis, IND. ENG. CHEM., **16**, 711 (1924).
(2) Kohman, *J. Phys. Chem.*, **33**, 226 (1929).
(3) Marzetti, *Rubber Age*, **13**, 433 (1923).
(4) Morris and Street, IND. ENG. CHEM., **21**, 1215 (1929).
(5) Ostwald, *J. Soc. Chem. Ind.*, **32**, 179 (1913).
(6) Venable and Fuwa, J. IND. ENG. CHEM., **14**, 139 (1922).

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Autographic Stress-Strain Curves of Rubber at Low Elongations[1]

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The usual methods of obtaining stress-strain data through the use of dumbbell-shaped test pieces and Schopper rings are briefly discussed. A new test piece is then described through the use of which stress-strain curves are drawn autographically, from which stresses are read quite accurately at the lower portion of the curve even down to 10 per cent elongation for either pure gums or heavily loaded stocks. Various factors affecting the position of the stress-strain curves are considered, such as variation in cures, speed of testing machine, temperature and humidity, together with the effect of mill grain and flaws in the test piece. There is also a brief discussion of the effect of increased loadings of carbon black.

INASMUCH as rubber compounders are devoting a considerable amount of laboratory work toward obtaining stress-strain data and discussing these data in detail in their technical papers, it would seem worth while that stress-strain measurements should be made with some accuracy. Furthermore, stress-strain measurements made to date do not give any information at low elongations of the test piece. The method here to be discussed furnishes a means of determining fairly accurately the stress at extremely low elongations. No attempt is made to correlate the shape of a stress-strain curve or the magnitude of the modulus derived therefrom with the practical service to be obtained from an article in which the rubber compound in question is used.

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Usual Methods of Obtaining Stress-Strain Data

A common method of obtaining data for constructing the stress-strain curve of rubber might be called the "hand and voice" method, in which two operators are employed, one following the bench marks of the dumbbell test piece with a ruler or pointers, and the other recording the dial load on receiving a verbal signal. Figure 1 shows such a test being made by two operators in an unusual position.

An improved one-man method makes use of the spark device by which a hole is burned through the recording paper by electrical contact made by the foot at each 100 per cent increment of elongation.

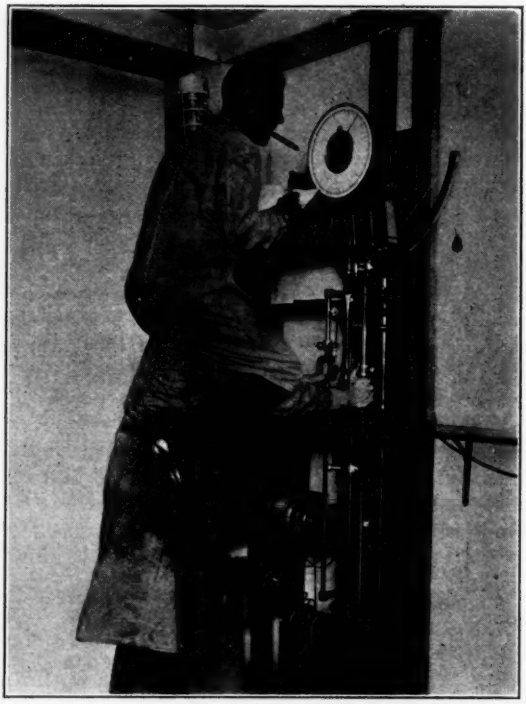

Figure 1—Obtaining Stress-Strain Data by a Common Method

Figure 2 shows a comparison of two stress-strain curves of a typical tire-tread stock made by each of these two methods. Notice that the curve made from data obtained by the two operators shows a higher modulus due to delay in recording the correct reading.

The Schopper method of employing a ring-shaped test piece gives an autographic curve to the breaking point, readable from about 200 or 300 per cent elongation upward, but not very accurate at lower elongations. Such curves have been obtained on rings 6 inches (15.2 cm.) in circum-

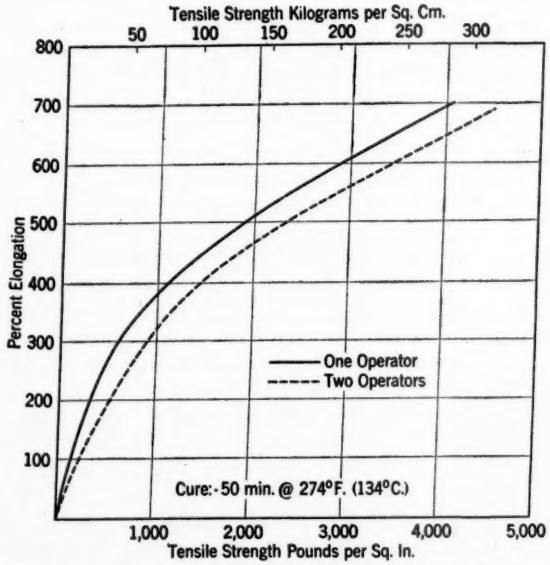

Figure 2—One Operator *vs.* Two Operators, Using Dumbbell Test Pieces and Tread Stock

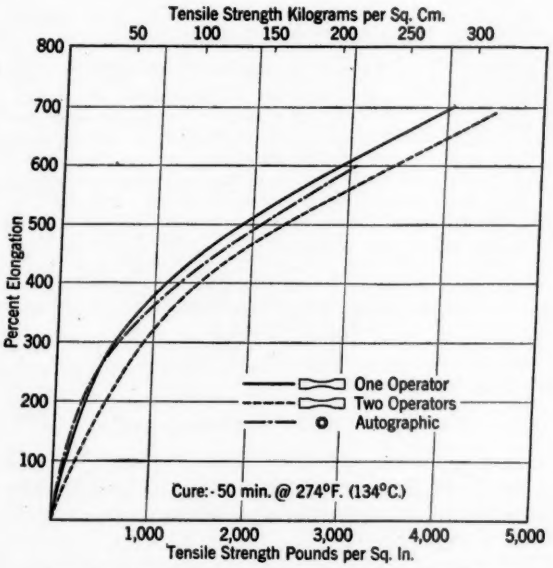

Figure 3—Dumbbell *vs.* Ring Test Piece, Tread Stock

ference slipped over four horizontal pulleys. Figure 3 shows the curve for the same tire tread stock in comparison with the two curves already given obtained on dumbbell test pieces. The curve breaks off short, showing the low tensile-stretch characteristics of ring test pieces.

New Test Piece

When a college freshman is given the problem of determining Young's modulus of steel, he may be handed a piece of wire 20 feet long. He attaches one end of the wire to a point near the ceiling and hangs increasingly heavy weights to the other end. He can read accurately the resulting increases in length of the wire by means of a finely divided scale read through a telescope. By this method a beginner obtains something very near the true value for Young's modulus. Is it surprising that various people testing rubber starting with a piece 1 inch (2.5 cm.) long get different results? It is true that rubber stretches much more than steel, so it is hardly necessary or feasible to start with a piece of rubber 20 feet long; but there is no reason why we cannot start with a piece of rubber 10 inches (25 cm.) long, and the results given in this paper have been obtained on a test piece of this length.

Figure 4

Actually the test piece in question is a loop 10 inches (25 cm.) long, or 20 inches (50 cm.) long if opened out, molded square 1/4 by 1/4 inch (6 by 6 mm.), as shown in Figure 4. It is stretched over single collar-button jaws. Such an enlarged test piece has the following advantages:

(1) It has about six times the cross section of the ordinary dumbbell or ring test piece, and therefore tends to overcome or mask friction of the machine, and for a very small elongation gives a relatively large reading in the dial.

(2) Each loop is molded, eliminating all subsequent cutting. The gage of the molded loop need not vary greatly, but if variation is found it may be compensated for by the adjustment of weight on the machine arm.

(3) Ordinary flaws in the molded loop are of no consequence.

(4) Every part of the test piece is stretching at a constant speed throughout the entire test.

Preparation of Rubber Compounds

Six compounds were prepared containing increased carbon black from pure gum up to 50 parts of black to 100 parts of rubber, according to the following formulas:

	A	A-1	A-2	A-3	A-4	A-5
Smoked sheets	50					
Pale crepe	50					
Zinc oxide	5					
Sulfur	3					

Antioxidant	1					
Stearic acid	0.75	1.5	2.25	3	3.75	4.5
Pine tar	0.75	1.5	2.25	3	3.75	4.5
Accelerator	0.5	0.6	0.7	0.8	0.9	1.0
Carbon black	..	10	20	30	40	50

In the mixing of these compounds A and A-5 were designed to cure at the same rate and then blended in the proper proportions to give the four intermediate compounds. All the compounds were designed to have the same rate of cure, and that this was actually the case is shown by the tensile-time curves in Figure 5. All the compounds reach their maximum tensile in about the same time. The 50-minute cure was chosen for the stress-strain curves shown below.

It might be well to point out that mixing two stocks in a

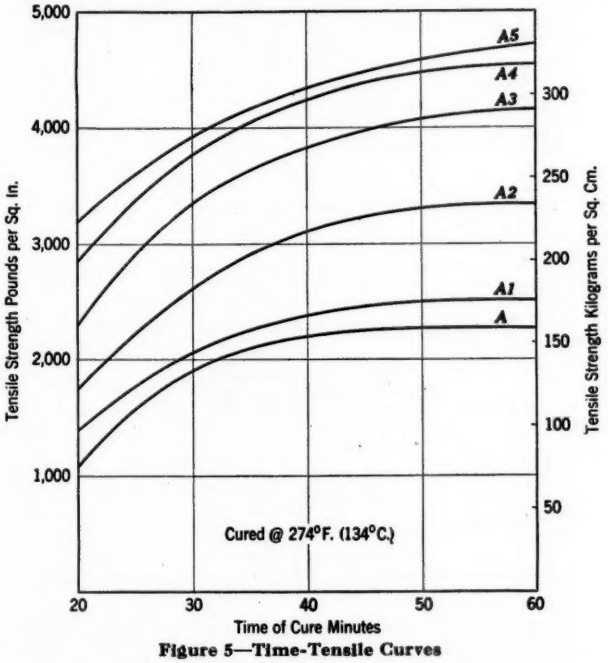

Figure 5—Time-Tensile Curves

50–50 ratio does not necessarily give a stock having physical properties exactly midway between those of the two individual stocks. In the above case the addition of 10 parts of carbon black produces less effect than might ordinarily be expected.

Factors Affecting Position of Curves

VARIATION IN CURE—Figure 6 shows the stress-strain curves of the pure gum compound at increasing cures drawn autographically using the 10-inch loop test piece. Figure 7 is the analogous series of curves for compound A-4, containing 40 parts of carbon black to 100 parts of rubber.

SPEED OF TESTING MACHINE—Figure 8 shows the effect of varying the speed of the testing machine on the stress-strain curve for pure gum, and Figure 9 is the analogous curve

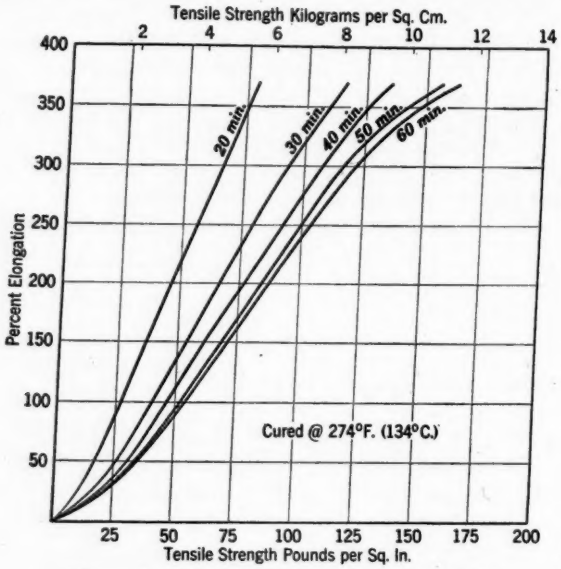

Figure 6—Effect of Increasing Cure, Pure Gum

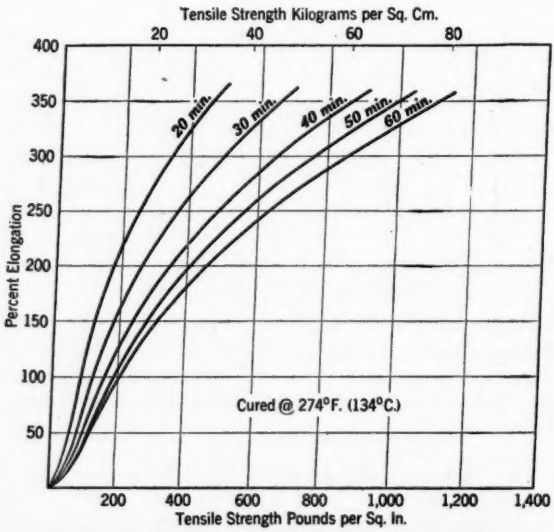

Figure 7—Effect of Increasing Cure, Tread Stock

for the tread stock containing 40 parts of carbon black. Note that in these cases the low speed of 2 inches (5 cm.) per minute gives the softer curves. Since with the 10-inch (25-

cm.) loop a stretch of 10 inches is required to give an elongation of 100 per cent it is clear that a speed of 20 inches (50 cm.) per minute for the machine is equivalent to a speed of

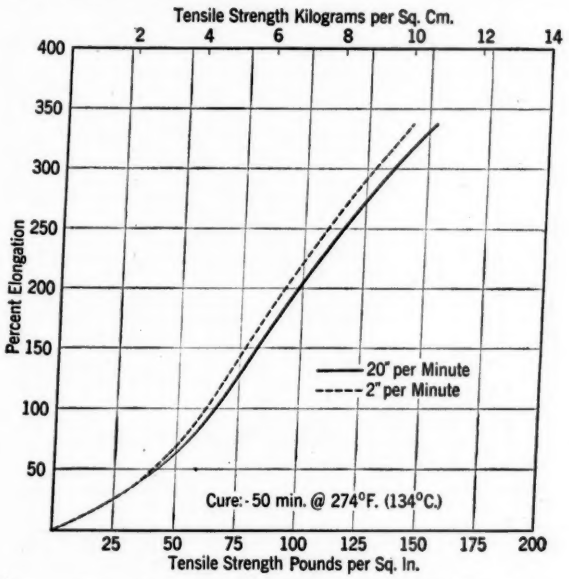

Figure 8—Effect of Machine Speed, Pure Gum

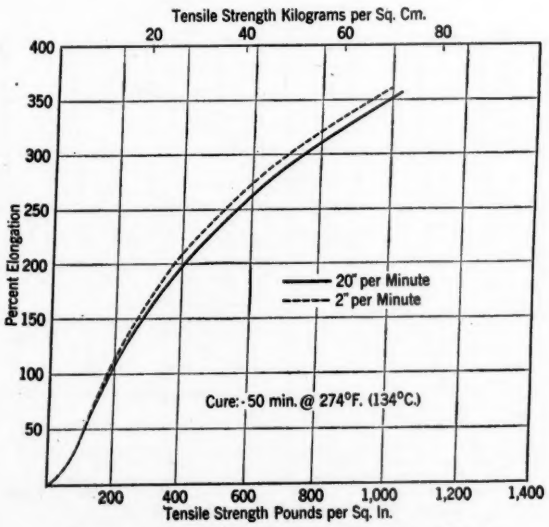

Figure 9—Effect of Machine Speed, Tread Stock

only 2 inches per minute for a 1-inch (2.5-cm.) length of the rubber sample, and that a speed of 2 inches (5 cm.) per minute for the machine is equivalent to only 0.2 inch (5 mm.) per

minute for a 1-inch (2.5-cm.) length. When dumbbell test pieces are stretched at the ordinary speed of 20 inches (50 cm.) per minute, the actual rate of separation of the 1-inch

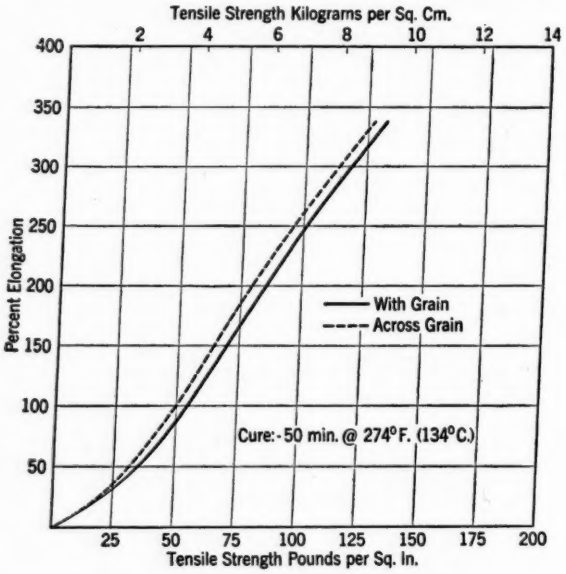

Figure 10—Effect of Mill Grain, Pure Gum

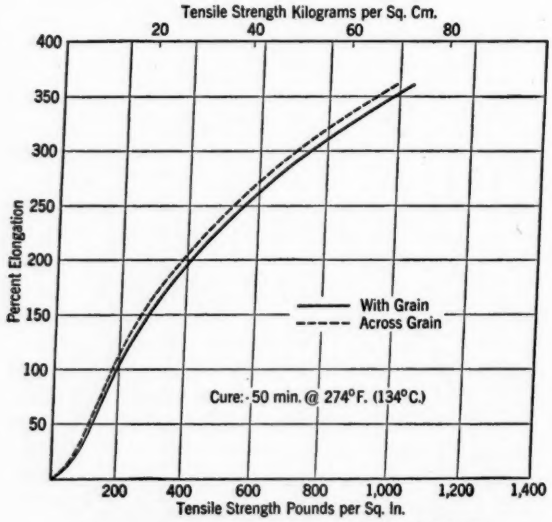

Figure 11—Effect of Mill Grain, Tread Stock

(2.5-cm.) bench marks begins at about half that speed and the rate of stretch of the 1-inch portion gradually decreases as the elongation increases. Therefore a 1-inch length of the

dumbbell test piece separates much faster than a corresponding length of a 10-inch (25-cm.) loop. All these considerations have a bearing on the relative position of stress-

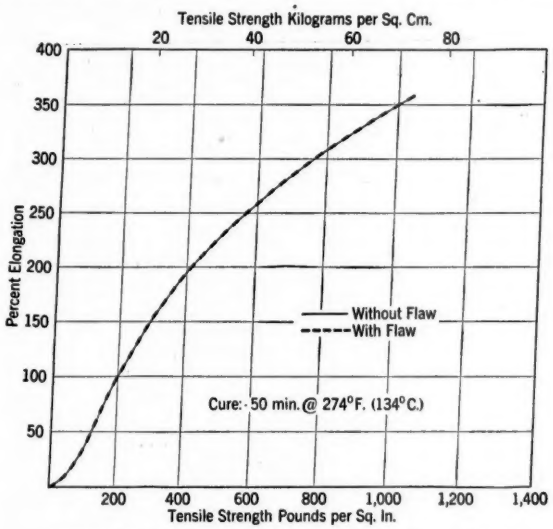

Figure 12—Effect of Flaw in Test Piece, Tread Stock

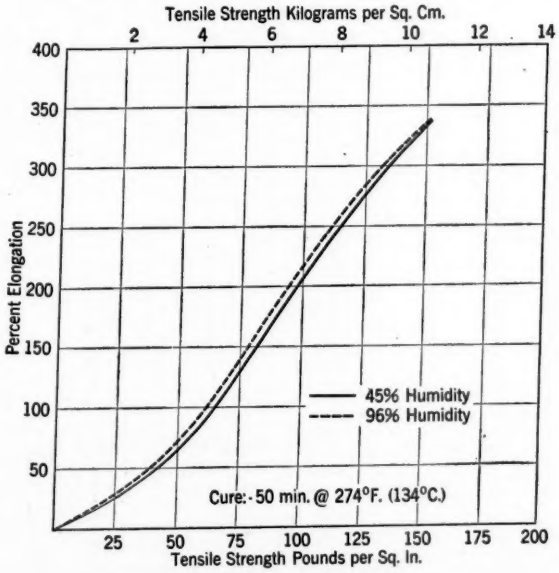

Figure 13—Effect of Humidity, Pure Gum

strain curves obtained on a compound at two different speeds. It is actually possible to obtain curves such that the one obtained at the lower speed indicates a stiffer stock than that obtained at the higher speed.

MILL GRAIN—Figures 10 and 11 show the effect of mill grain on the stress-strain curves of pure gum and tread stock, respectively. The curves obtained show that the stocks are

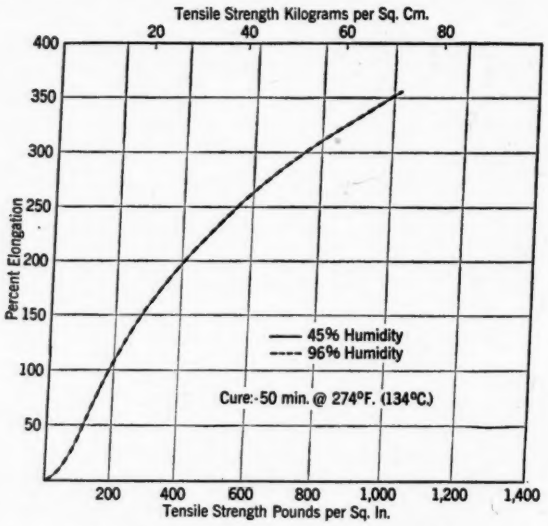

Figure 14—Effect of Humidity, Tread Stock

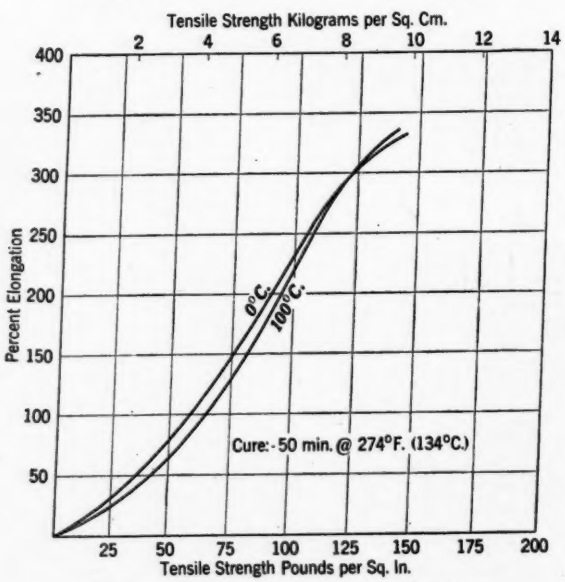

Figure 15—Effect of Temperature, Pure Gum

slightly stiffer when the loops are cut in a direction lengthwise with the grain.

FLAWS IN TEST PIECE—Figure 12 shows two curves, one

obtained with a perfect loop and the other with a loop containing severe flaws. It is evident that the flaws do not appreciably influence the shape or position of the curve in any way.

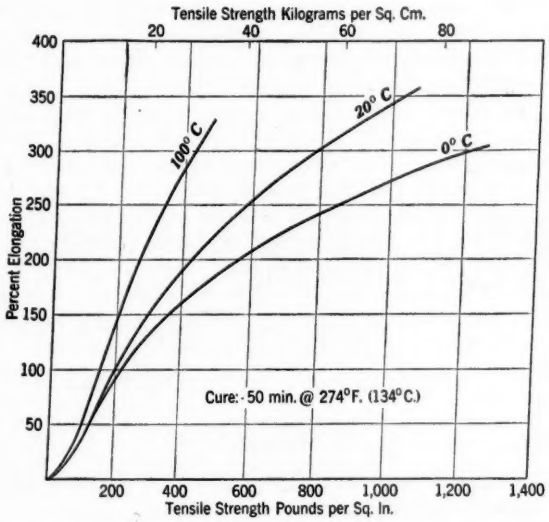

Figure 16—Effect of Temperature, Tread Stock

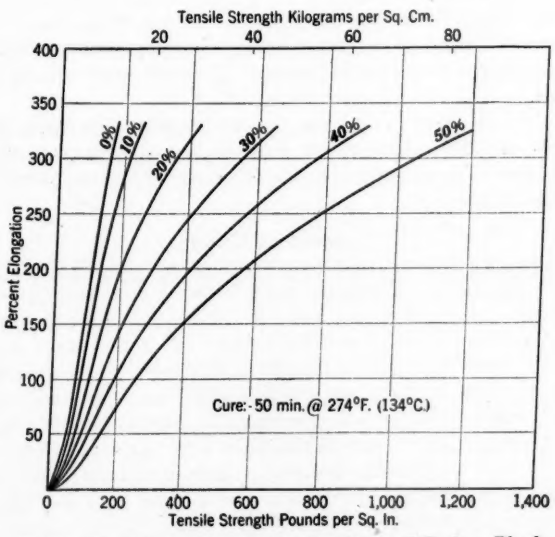

Figure 17—Effect of Increasing Loadings of Carbon Black

HUMIDITY—Figures 13 and 14 show curves for pure gum and tread stock, respectively, run at two different humidities, 45 and 96 per cent. The effect of humidity is nearly negligible. A relative humidity of 45 per cent is one of the con-

ditions adopted as standard by the Physical Testing Committee for conditioning the test samples and it does have an effect on uncured stock.

TEMPERATURE—Figures 15 and 16 show curves for pure gum and tread stock, respectively, drawn at three different temperatures. As previously pointed out (*1*), a loaded compound shows considerable spread between the 0° and 100° C. stress-strain curves, whereas a properly cured pure gum stock may show very little, if any, spread, and may even show a crossing of these two curves whereby the stress at 100° C. is actually greater at a given elongation than the stress at 0° C. Figure 15 shows that the pure gum compound being tested has practically identical stress-strain properties at the two temperatures up to an elongation of at least 300 per cent.

INCREASED LOADINGS OF CARBON BLACK—Figure 17 shows the effect as indicated by stress-strain curves of increasing loading of carbon black. The 50-minute cure was chosen for each of the six compounds in molding these test pieces. It is to be noted that stresses can be read at elongations as low as 10 per cent.

Conclusions

(1) Ring or loop test pieces permit autographic records to be drawn at constant speed.

(2) A longer, larger test piece permits more accurate results to be obtained.

(3) The effect of temperature of the test room is most important; speed of testing machine and direction of mill or calendar grain in sample less so; effect of relative humidity is nil.

(4) The 10-inch (2.5-cm.) loop test piece described gives fairly accurate stress-strain data at low elongations, which probably is within the field approaching the action of rubber goods in service.

Literature Cited

(1) Somerville and Cope, *India Rubber World* (November, 1928); *Trans. Inst. Rubber Ind.*, **4**, 263 (1928).

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Application of the Falling Cylinder to the Measurement of the Viscosity of Thick Rubber Cements[1]

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It has been shown that the time of fall, t, of cylinders through many thick cements can be represented with reasonable accuracy by the equation

$$dt = k \cdot \frac{d(x^2)}{(W - \pi r^2 \rho x)^n}$$

or in the integrated form

$$t = k \frac{x^2}{W^n}\left[1 + \frac{2n}{3}\frac{\pi r^2 \rho x}{W} + \frac{2n(n+1)}{4 \cdot 2!}\left(\frac{\pi r^2 \rho x}{W}\right)^2 + \frac{2n(n+1)(n+2)}{5 \cdot 3!}\left(\frac{\pi r^2 \rho x}{W}\right)^3 + \cdots\right]$$

where ρ is the density of the cement, n is a constant of the cement, and k is a constant independent of the distance fallen, x, and the weight, W, but varies with the cement being tested and the radius of the cylinder used. This equation was tested with cylinders varying from 0.0487 to 1.32 cm. in diameter in liquids having viscosities ranging from that of castor oil (viscosity 6.5 poises) which gave $k = 0.007$ to that of a pigmented stock which gave $k = 0.90$ for a cylinder having a diameter of 0.122 cm.

A 15 per cent suspension of clay in mineral oil, in contrast with rubber solutions, showed a definite yield value and also anomalous turbulence.

Falling-cylinder viscometers using steel cylinders were designed for use in control testing, and simplified equa-

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tions were developed for their use. These were found satisfactory for cements having viscosities ranging from about that of U. S. Bureau of Standards Standard Oil No. 7 (49.2 poises) where $k = 0.0486$ to cements giving values of k about 50 times as large, and values of n up to about 1.5. It was found that the thicker cements made from only slightly milled rubber did not follow the law upon which the above equations were based, so the falling-cylinder viscometers did not give consistent values of n and k. Even in these cases, however, the viscometers can be used for control testing, provided only that the shearing force at the surface of the cylinder is not greater than the adhesion of the cement to the cylinder surface.

The steel viscometers have been used in testing asphalts having viscosities up to about 900,000 poises. They should be useful in studying other materials, since the readings are easy to make, and can be taken at several shearing stresses, and they can be used in opaque as well as transparent liquids having a wide range of flowing properties.

THE need for simple, rapid, and accurate means of measuring the flowing properties of viscous, semi-solid materials is apparent, but the difficulties involved in the development of such an instrument are considerable. One of the chief difficulties is that most of these materials do not follow Poiseuille's law, and consequently no device which measures the force caused by a single rate of shear, or vice versa, will give data from which a general expression of the law of flow may be derived. When the relation of rate of shear to force is unknown, it can be determined by measuring the rates of shear for a large range of forces in instruments such as the MacMichael or Couette viscometers, or the Bingham variable-pressure viscometer, but this procedure is not economical for testing a large number of samples, as in factory control work.

For many solutions of lyophilic colloids a law of the type

$$S = KP^n \qquad (1)$$

where S is the rate of shear, P is the shearing stress, and K and n are constants, has been found to hold [see (*4*) and (*5*) for summary of work in this field]. Herschel and Bulkley (*2*) showed that this relation held for rubber solutions except at high concentrations, where the equation

$$S = K(P - p)^n \qquad (1a)$$

expressed the facts more accurately, p being a small constant. If Equation 1 is valid, it is theoretically possible to determine the constant K and n, and so the complete law of flow, by two measurements in a MacMichael or Bingham variable-pressure viscometer. However, for use in control testing both these instruments have serious disadvantages, such as the difficulty of cleaning, the time required to make the test, and under some conditions the inaccuracy of the results.

An attempt was made to measure the constants of this flow equation by other means which were free from some of these disadvantages. Because of its extreme simplicity, the method of measuring the times of fall of a long cylinder through the surface of cements would make a very satisfactory method of measuring the flowing properties of such materials, provided the measurements could be interpreted in terms of the fundamental constants of Equation 1. To do this rigorously one would have to have the complete solution of the hydrodynamic problem of the fall of a cylinder in a liquid for which Poiseuille's law did not hold. While this general problem was not solved, it was found possible by a semi-empirical method to express the time of fall of a cylinder in terms of the distance fallen, the force acting on the cylinder, and the two constants, n and K, of Equation 1. It was found that n was independent of the radius of the falling cylinder, but this was not true for K. The relation between K and the radii of the falling cylinder and container could not be determined from the theory, so it had to be obtained empirically by calibration against liquids of known viscosities.

The results were tested with cylinders of different diameters, each with a number of different weights, in various rubber cements giving a range in time of fall from 10 to 1200 seconds. Castor oil and a 15 per cent suspension of clay in mineral oil were also tested. The equations were found to hold in all cases except for the thickest cements made from unmilled rubber and for the clay suspension.

Derivation of Formula

When a solid cylinder having its axis perpendicular to the surface of a liquid falls at a rate sufficiently slow that turbulence and surface effects are negligible, there is a telescopic flow of the liquid past the cylinder. This may be considered a slipping past each other of concentric shells of liquid, similar to the flow in a capillary tube. In the latter case, however, the pressure is constant over the cross section of the capillary, and consequently the force causing the motion increases as the radius of the shell increases; while in the case of the falling cylinder the force acting on each shell is equal to the force acting on the solid cylinder, so that the shearing stress decreases with increasing radius. If r_0 is the radius of a solid cylinder and x the distance it is immersed in the liquid, then $\dot{x}_{r_0}$ $(= dx_{r_0}/dt)$ is its velocity, and $\dot{x}_r$ is the downward velocity of a particle at a distance r from the axis of the cylinder. The rate of shear, S_r, or the velocity gradient normal to the surface of the cylinder, will be $d\dot{x}_r/dr$, and the velocity of the cylinder will be the integral of the velocity gradient from r_0 to R, the radius of the container, or

$$\dot{x}_{r_0} = \int_{r_0}^{R} S_r dr \qquad (2)$$

If Equation 1 is valid, and we can neglect inertia effects, S_r will be proportional to the n^{th} power of the shearing stress. This actual stress cannot be determined exactly, however, as the flow lines are not all parallel to the axis, but we can write

$$S_r = K \cdot \frac{F^n}{f(x, r)} \tag{3}$$

where F is the force acting on the cylinder. If we assume that the function $f(x, r) = f_1(x) . f_2(r)$, then from (2)

$$\dot{x}_{r_0} = \frac{KF^n}{f_1(x)} \int_{r_0}^{R} \frac{dr}{f_2(r)} = \frac{KF^n}{f_1(x)} \cdot \phi\ (R, r_0) \tag{4}$$

To find x as a function of the time t one must know the function $f_1(x)$. While there are some grounds for expecting that $f_1(x) = x^n$, it was found that the simpler relation $f(x) = x$ gave results in better agreement with experiments.

Substituting this in Equation 4 we have

$$\frac{dx_{r_0}}{dt} = \frac{KF^n}{x} \cdot \phi\ (R, r_0)$$

which on rearranging and dropping the subscript in (dx_{r_0}/dt) gives

$$2xdx = CF^n dt \tag{5}$$

where $C = 2K\phi(R, r_0)$. C may also be a function of the exponent n. It would be very desirable to have a more detailed analysis of this factor, but this could not be made in the present work. If F^n were independent of x, Equation 5 would give the relation $x^2 = c't$ for a given cylinder and liquid. This does not hold because of the buoyant effect. To allow for this, one may write

$$F = (W - \pi r_0^2\ \rho x) = (W - ax)$$

where W is the weight of the solid cylinder, x is the depth immersed, ρ is the density of the liquid, and $a(= \pi r_0^2 \rho)$ is the weight of liquid displaced when the cylinder is immersed one centimeter. This ignores surface tension effects and the depression of the surface around the cylinder, but it was found that these did not cause any serious error except with the very thickest cements.

Substituting in (5) and rearranging gives

$$\frac{d(x^2)}{(W - ax)^n} = Cdt \tag{5a}$$

Expanding $(W - ax)^{-n}$ into a power series and integrating yields

$$W^{-n}x^2 + 2/3\ nW^{-(n+1)}ax^3 + \frac{2n(n + 1)W^{-(n+2)}}{2! \cdot 4} a^2x^4 + \frac{2n(n + 1)(n + 2)}{3! \cdot 5} W^{-(n+3)}a^3x^5 + \ldots = Ct \tag{6}$$

if $x = 0$ when $t = 0$. On rearranging and putting $k = 1/C$ one gets

$$t = k \cdot \frac{x^2}{W^n}\left[1 + \frac{2n}{3}\frac{ax}{W} + \frac{2n(n+1)}{2!\,.\,4}\left(\frac{ax}{W}\right)^2 + \frac{2n(n+1)(n+2)}{3!\,.\,5}\left(\frac{ax}{W}\right)^3 + - -\right] \quad (7)$$

It is seen that the part of the equation in the brackets is a power series in (ax/W) which is the ratio of the buoyant force, ax, to the weight, W. When this ratio is small, only the first term need be taken, and the time of fall becomes proportional to the square of the distance fallen. If the ratio $ax/W < 1$ the series is convergent for all values of n, but if the buoyant force becomes equal to the weight making

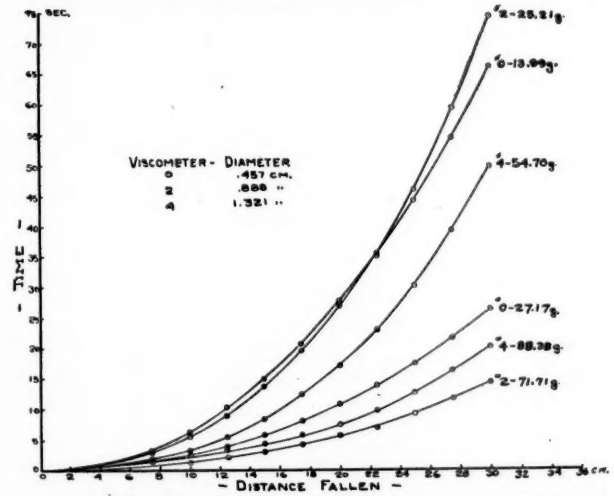

Figure 1—Fall of Cylinder through Cement A-1—25° C.

the ratio $ax/W = 1$, the series is no longer convergent, and the time of fall becomes infinite—i. e., the cylinder floats.

If this equation is valid for a considerable range of values of W, x, and r, it would be possible to determine the fundamental constants of the cement very easily by measuring the time of fall of cylinders through the cement. To see how far the assumptions upon which Equation 7 was based were valid, the following tests were made.

Experimental Tests

The cylinders used were glass tubes about 35 cm. long and from 0.0487 to 1.32 cm. in diameter. They were sealed at one end and were loaded with various amounts of mercury to give different weights for cylinders of the same radius. By means of a scale fastened inside the tube the distance

immersed could easily be read, and the time of fall was recorded at 2.5-cm. intervals over the range from 0 to 30 cm. A smooth guide slightly larger than the falling cylinder was placed a few centimeters above the liquid to make the cylinder fall vertically. The cement to be tested was placed in a 2-liter cylinder 7.5 cm. in diameter. Later tests were also made with the cement in larger containers, and steel needles 0.086 cm. in diameter and about 20 cm. long were used.

Rubber Cements—Figure 1 shows a typical set of curves giving the relation of time of fall to distance fallen at 25° C. in one of the thicker compounded cements (A–1) containing rubber 14.5, rosin 1.0, zinc oxide 4.3, and gasoline 48.0 parts by weight, and having a density of 0.792. Cylinders of three different radii and two weights each were used. The data give a set of approximately parabolic curves. To get

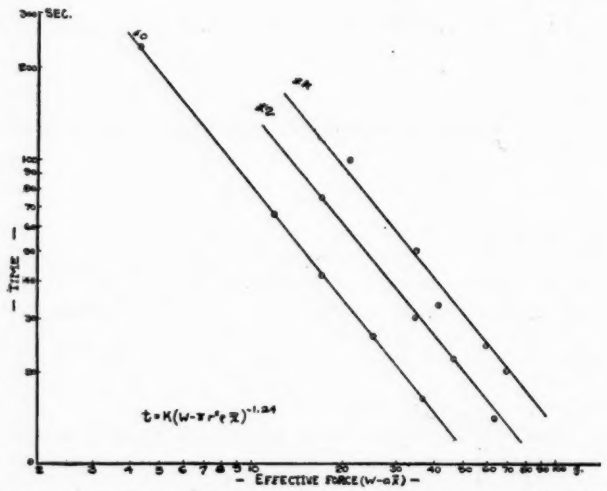

Figure 2—Relation of Time of Fall in Cement A-1 to Effective Force

the exponent n of Equation 5 from the observed data, the time of fall for 30 cm. is plotted on a log-log scale against the effective force for several weights of each cylinder, and the slopes of the lines determined as shown in Figure 2. The effective force acting on the cylinder is taken as the weight minus the average buoyant force over the time of fall ($W - a\bar{x}$). This is not quite correct, since it ignores the exponent in the buoyancy term, but where this term is relatively small it does not cause any appreciable error. It is seen from Figure 2 that a straight line is obtained for a tenfold change in ($W - a\bar{x}$) for the smaller cylinder, and that cylinders of different sizes give curves having about the same slope, and therefore the same value for n—namely, 1.24. Substituting this value in Equation 7 gives the relation

$$= k \cdot \frac{x^2}{W^{1.34}}\left[1 + 0.826\left(\frac{ax}{W}\right) + 0.695\left(\frac{ax}{W}\right)^2 + 0.601\left(\frac{ax}{W}\right)^3 + - -\right] = k \cdot f(\rho, x, W)$$

The observed times of fall for various distances and weights were then plotted against the corresponding values of $f(\rho, x, W)$ calculated from this equation, with the results shown in Figure 3. It is seen that the points for each cylinder fall on straight lines, showing that k is a constant for any one cylinder and that Equation 7 is valid over this range. For this cement k is nearly proportional to the radius of the viscometer, but this relation does not hold for other cements. A sample of cement (A–2) with a composition similar to A–1 was tested at 25° and 42° C. with a set of cylinders covering a larger range of diameters. Figure 4 shows the times of fall at 25° C. plotted against the corresponding values of the $f(\rho, x, W)$. In this case the value of n was found to be 1.10, and it was about the same (1.12) at 42° C. As would be expected, the values of k for the different cylinders decrease with increasing temperature as shown in Table I.

Table I—Effect of Temperature on the Viscosity of a Compounded Cement A-2

Cylinder	Diameter	Min. Wt.	Time of Fall at 25° C. with Min. Wt.		k	
					25° C.	42° C.
	Cm.	*Grams*	*Sec.*	*Cm.*		
N	0.122	0.7967	1185	27.5	0.90	0.88
P	0.267	2.513	453	30.0	..	1.20
0	0.457	6.001	450	30.0	1.75	1.55
1	0.584	18.990	98	30.0	2.04	1.89
4	1.321	41.414	215	30.0	5.20	4.29

To see if the falling-cylinder method could be applied to the less viscous cements, a pure-gum cement (B) containing 6 per cent by weight of Para rubber in benzene was tested at several temperatures. The cylinders of larger diameter used above were not suitable for this cement, as they fell so rapidly that the time intervals could not be measured accurately, and inertia and turbulence effect probably were relatively large. Thinner cylinders were found satisfactory, however, and they gave straight lines when the times of fall of any cylinder for various distances and weights were plotted against the corresponding values of the function $f(\rho, x, W)$ given by Equation 7, showing that the equation held for this cement also. The effect of temperature on the constants is given in Table II. It is seen that both n and k decrease with temperature.

Castor Oil—Since castor oil is commonly used to standardize viscometers, it was tested by this method. It is known that for this liquid the rate of shear is proportional to the force, so the value of n is 1, and Equation 6 becomes

$$\frac{2xdx}{(W - ax)} = Cdt \qquad (8)$$

or, putting $k' = 2/c$,

$$t = k' \int \left[-1/a + \frac{W}{a(W - ax)} \right] dx$$
$$= k' \left[-\frac{x}{a} - \frac{W}{a^2} \log (W - ax) \right] + C'$$

When $x = 0$, $t = 0$, so $C' = (k'W/a^2) \log W$. After simplifying,

$$t = k' \left[-\frac{x}{a} - \frac{W}{a^2} \log\left(1 - \frac{ax}{W}\right) \right] \qquad (9)$$

This appears very different from the equation one would get by substituting $n = 1$ in Equation 7 above. However, on expanding $\log (1 - ax/W)$ into a power series and simplifying,

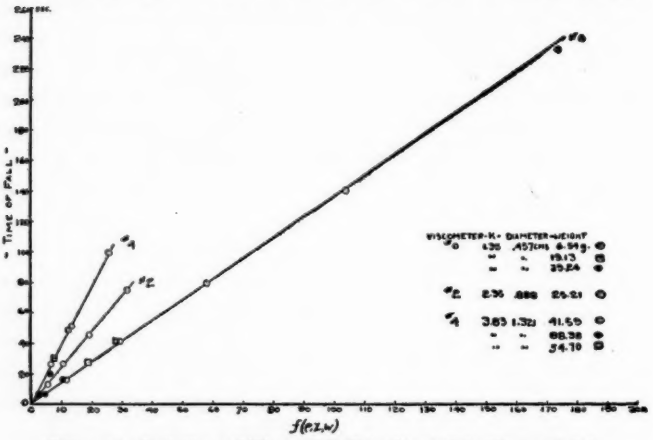

Figure 3—Relation of Time of Fall to $f(\rho,x,w)$ in Cement A-1
$t = k \cdot f(\rho,x,w) = k\ x^2/w^{1.34}[1 + 0.826\ ax/w + 0.695(ax/w)^2 + 0.601(ax/w)^3 + \ldots]$

the two equations become identical. The exact solution given by Equation 9 is not suitable for practical use, since it becomes indeterminate when a is zero. and when a is small the density must be known very accurately.

Table II—Effect of Temperature on Constants of a Pure-Gum Cement

Cylinder	Diameter	25° C.		39.5° C.		48° C.	
		n	k	n	k	n	k
	Cm.						
N	0.122	1.276	0.056	1.205	0.041	1.148	0.040
M	0.172	1.276	0.065	...	...	...	...
P	0.267	1.276	0.087	1.205	0.067	1.148	0.055

To get sufficiently large times of fall, cylinders of very light weight and small diameter (0.0487 to 0.172 cm.) had to be used. It was found that for this range of diameters the data could all be expressed by the equation

$$= 0.0142 \cdot r^{0.236} \frac{x^2}{W}\left[1 + 2/3\,\frac{ax}{W} + 2/4\left(\frac{ax}{W}\right)^2 + 2/5\left(\frac{ax}{W}\right)^3 + - -\right] = 0.0142 \cdot r^{0.236} f(\rho, x, W) \quad (10)$$

which is the equation of the straight line in Figure 5, where the points give the observed times of fall plotted against the corresponding values of the function $r^{0.236} f(\rho, x, W)$. Since the absolute viscosity, η, of castor oil at 25° C. is 6.51 poises (*6*), we can write for cylinders of this range of radii in this material,

$$1/\eta = \frac{0.00218}{t} \cdot r^{0.236} \cdot \frac{x^2}{W}\left[1 + 2/3\,\frac{ax}{W} + 2/4\left(\frac{ax}{W}\right)^2 + 2/5\left(\frac{ax}{W}\right)^3 + - -\right] \quad (11)$$

Comparison of Results—Since the relation between the k values obtained with cylinders of different radii in a given cement could not be determined from the fundamental equation, and the empirical relations which were observed held over only relatively small ranges, different liquids can best be compared by testing with the same cylinder. Table III gives a comparison of the data obtained on the liquids at 25° C. with cylinder N of 0.122 cm. diameter.

Table III—Comparison of Data on Liquids at 25° C. with Cylinder *N* of 0.122 cm. Diameter

Liquid	Time of Fall (25 cm.) with Weight of 0.7967 Gram	n	k
	Seconds		
Cement A-2	941.8	1.10	0.90
Cement B	64.2	1.28	0.056
Castor oil	7.3	1.00	0.0071

It is seen that the constant n does not always parallel k. Later work showed that for rubber solutions n depends very much on the amount of milling the rubber receives and is some measure of the elasticity of the cement. The results show that under these conditions a falling-cylinder viscometer can be used for cements and oils having a range of over 130 fold in the time of fall, and the constants n and k may be used to characterize the flowing properties of the material.

Clay-Oil Suspension—To see what sort of results would be obtained with falling-cylinder viscometers in an entirely different type of material, for which Equation 7 is not valid, a 15 per cent suspension of clay in mineral oil was studied. Bingham's law would be expected to hold for this material, and to verify this it was tested with the MacMichael viscometer. The results shown in Figure 6 are rather erratic, but they indicate that this law holds fairly well; although, probably because of seepage, no yield value could be measured when the speed of the outer cylinder was reduced to zero.

The curves giving the relation between the time of fall and the distance fallen for three cylinders of the same radius ($r = 0.292$ cm.) but different weights, shown in Figure 7, are rather surprising. For the cylinder of lightest weight (12 grams) the relation of the velocity of fall v (tangent of curve 1) to the distance fallen is given fairly accurately by the equation

$$v = k \cdot \frac{F - f}{A} = C\left[\frac{W - f}{x} - a\right] \qquad (12)$$

where F is the force equal to $(W - ax)$, f is the yield value, A $(= 2\pi rx)$ is the area of cylinder below the surface of the material, and C is equal to $k/2\pi r$, as would be expected if Bingham's law were valid. The cylinder came to a stop

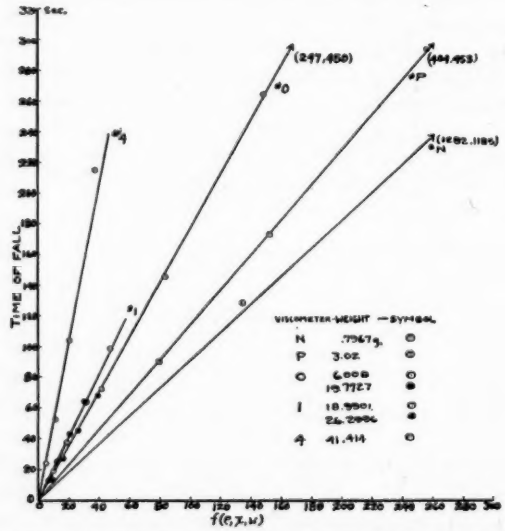

Figure 4—Relation of Time of Fall to $f(\rho,x,w)$ in Cement A-2—25° C.

$t = k \cdot f(\rho,x,w) = k\, x^2/w^{1.10}[1 + 0.7333\ (ax/w) + 0.5775\ (ax/w)^2 + \ldots]$

at 16 cm. when the force F was 8 grams, giving a value of f/x of 0.50. With the next larger weight the cylinder acted somewhat differently (curve 2). It fell very rapidly for 10 cm., then fell with a nearly constant velocity to about 20 cm., after which the velocity decreased, reaching zero at about 28 cm. when $(W - ax)$ was 13.5 grams. This gives the same value of (f/x) as found with the lighter weight.

With the largest weight (curve 3) the cylinder fell very rapidly for about 15 cm. and then fell at a nearly constant velocity for the rest of its length. This was at first thought to be due to the momentum acquired during the first 15 cm. fall. However, it was shown that this is not the case by immersing the cylinder various distances up to 20 cm. and

then allowing it to fall freely the rest of the way. The time-distance curves (3*a* and 3*b*) are straight lines which are practically parallel to the straight part of curve 3. If most of the resistance to the fall occurs at the end of the cylinder—i. e., the cylinder essentially pushes a hole through the suspension—one would expect the velocity of fall to be nearly constant. This cannot be the correct explanation, however, in view of the results for the lightest weight (curve 1), and also because, for cylinders of different radii and the same weight, the velocity does not vary inversely as the square of the radius. The most plausible explanation seems to be that the clay suspension shows turbulence, since the high yield value causes most of the shear to take place in a thin layer close to the falling cylinder, making the rate of shear extremely high. This makes the resistance increase much faster than

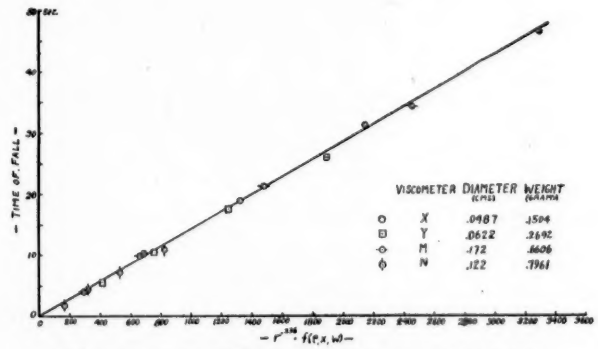

Figure 5—Fall of Viscometers in Castor Oil at 25° C.

$$i = 0.014 \cdot r^{0.336} \cdot x^2/w[1 + 2/3\,(ax/w) + 3/4\,(ax/w)^2 + 2/5\,(ax/w)^3 + \ldots]$$

the velocity, thus tending to keep the velocity of fall constant. This may be similar to the anomalous turbulence which Hatschek found for ammonium oleate gels (*1*).

Practical Viscometers

The above work showed that the flowing properties of rubber cements could be determined under certain conditions with falling-cylinder viscometers. For practical factory use, however, glass viscometers have the disadvantage that they are easily broken, the tall graduates used for holding the cement are not easy to clean, the density of the cement must be known, and considerable calculation is required to get the n and k factors. To avoid these objections a series of cylinders (numbered 1, 2, 3, and 4) were constructed, using knitting needles or hardened steel wires 0.086 cm. in diameter and about 20 cm. long with various weights fastened to the upper ends. The weights were adjusted so that the average forces $(W - a\bar{x})$ on the various cylinders were in the ratios 1:2:4:8. It can be shown that when ax/W is much less than 1 the

average buoyant force acting during a given fall, x, is very nearly two-thirds the buoyant force acting at the end of the fall, or $a\bar{x} = 2/3\,ax$. This relation was used in determining the force. Because steel was used for the cylinders, the maximum buoyant force was relatively small, and it could be assumed that the density of all the cements was 0.8 without making an error of more than about 1 per cent in the results if the actual densities range from 0.6 to 1.0. These cylinders were allowed to fall through a smooth guide which kept them vertical. The guide was split longitudinally, the halves being fastened to the jaws of a spring clamp which allowed the viscometer to be removed after a test without getting cement in the guide. By means of a rack-and-pinion adjustment the

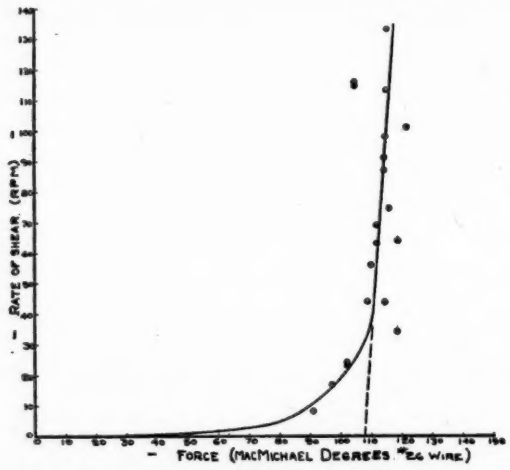

Figure 6—Test of Clay-Oil Suspension in MacMichael Viscometer

guide was always set at a definite height above the surface of the cement, and the cylinders were marked with a scale such that the distance immersed could be read directly as the scale passed the top of the guide. The time required for a fall of 15 cm. was measured with a stop watch. Surface evaporation was kept as small as possible and the surface film was removed just before making a test.

From the time of fall of cylinders 1 and 2, or 2 and 3, or 3 and 4, the value of n may be computed from the formula

$$n = \frac{\log t_1/t_2}{\log F_2/F_1} = 3.32 \log (t_1/t_2) = 3.32 \log (t_2/t_3), \text{ etc.} \quad (13)$$

since $(F_2/F_1) = (F_3/F_2) = 2$. The subscripts refer to the number of the cylinder. After n has been obtained k may be found from the equation

$$\log k = (\log t_1 - 2 \log 15 + n \log F_1), \text{ etc.}$$

or

$$k = \log^{-1}(\log t_1 - 2.3522 + n \log F_1) \qquad (14)$$

These equations follow from the integration of Equation 5*a*, assuming that the force $(W - ax)$ is a constant over the 15-cm. fall, equal to $(W - 10a)$, which gives, instead of Equation 6, the result

$$t = k\, x^2\, (W - 2/3\, ax)^{-n} \qquad (15)$$

or, when $x = 15$,

$$t = 225\, k(W - 10a)^{-n} \qquad (15a)$$

The practical determination of n and k was simplified by the use of tables prepared from these formulas. The cylinders were tested by means of several cements and a sample of U. S. Bureau of Standards Standard Oil No. 7, and found to give consistent results. Since the results are independent of

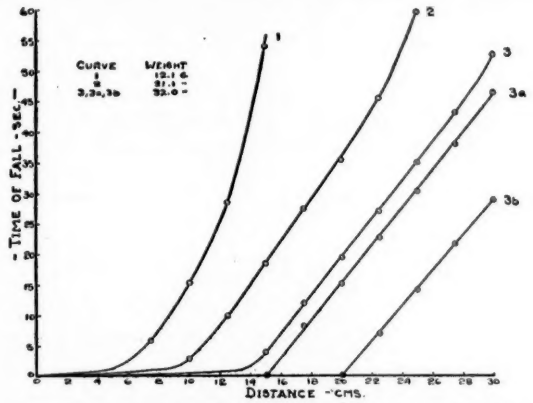

Figure 7—Fall of Cylinder Viscometer ($r = 0.292$ cm.) in Clay-Oil Suspension

the size of the container, provided its diameter is greater than 15 cm., the viscometers may be used in large drums, making it unnecessary to remove a sample for the test. Wherever possible the same cements were also tested with steel cylinders of 0.170 cm. diameter; and it was found that both sizes gave the same value of the constant n although the value of k varied with the radius. The results for U. S. Bureau of Standards Standard Oil showed that the absolute viscosity was about 1000 times the value of k for the cylinders of 0.086 cm. diameter.

On testing some cements containing about 11 per cent of only slightly masticated rubber, it was found that consistent results could not be obtained with different weights of the steel cylinders; in some cases the values of n varied from 1.3 to 1.6. The larger glass cylinders gave equally inconsistent results, indicating either that the surface effects were too great to be neglected or that the law given by Equation 7 did not hold for this cement. Both of these factors probably enter, for on testing the cement with the MacMichael vis-

cometer at various speeds and plotting the logarithms of the deflection, F, against the logarithm of the speed Ω to get the value of n in the equation

$$F^n = K \cdot \Omega^n$$

it was found that n was not a constant, but increased with increasing speeds. Because of the tendency of these thick cements to climb on the center cylinder during a run, it was difficult to get accurate readings; but in general the values of n obtained over the range of 10 to 50 r. p. m. were somewhat higher than those obtained with the falling-cylinder viscometer, while at speeds of 1 to 10 r. p. m. the MacMichael n values were about the same or somewhat lower than the n values obtained with the falling-cylinder viscometers.

To see if the inconsistent results were due to the fact that the rubber had been milled only slightly, rubber was milled 5, 15, and 30 minutes on a laboratory mill, and cements were made from each lot to a concentration of 21 per cent, using naphtha as solvent. The plasticity of the rubber was determined with the simplified Goodrich plastometer (*3*). The data obtained for these solutions are shown in Table IV.

Table IV—Effect of Milling Rubber on Viscosity Constants of Its Solutions

Cement	Time of Milling	Plasticity of Rubber	Steel Cylinders Diam. = 0.086 cm.		Glass Cylinders Diam. = 1.106 cm.	
	Min.		n	k	n	k
1	5	6.8	(1.58–1.68)	(10.10–13.98)	(1.61–1.73)	(260–310)
2	15	26.8	1.14	0.146	1.18	0.722
3	30	53.3	1.07	0.045	1.11	0.188

It is seen that the values of n and k for cement 1 are not constant for either cylinder. Cements 2 and 3 show much more consistent results, indicating that the more the rubber is masticated the more nearly Equation 7 is valid. The value of n for these cements could be checked within ± 0.03, and k could be checked to within about 5 per cent.

The value of the exponent n cannot be determined with any degree of accuracy when the ratio of forces used is less than 2, or when the time of fall for 15 cm. is less than 10 seconds, so the steel cylinders could not be used to test a 21 per cent solution of rubber masticated 90 minutes, the plasticity of which was 79.8. However, this solution probably had a value of n very near 1, and it was thin enough that it could be tested with sufficient accuracy in a viscometer of the Ostwald type.

These viscometers have also been used to test asphalts both at the temperature of boiling water and at room temperature, and in all cases the fall of the viscometers could be represented by Equation 7 above. Since there is no trouble with evaporation in these materials, they can be

tested quite satisfactorily even though the times of fall are nearly an hour for a distance of 5 cm. with the heavier weights. It was found that at 25° C. the values of n for these asphalts were usually close to 1.0, while the values of k ranged from 300 to 900, giving viscosities from 300,000 to 900,000 poises.

These results indicate something of the possibilities of using this type of viscometer in development as well as in control work. In the latter type of work the instruments may, of course, be used for setting up empirical standards for a material even though the law of flow given by Equation 7 is not valid. Where the law does hold, two simple tests will determine the constants of the equation, allowing one to calculate the flowing properties of the material over a rather wide range of shearing stresses.

Literature Cited

(1) Hatschek, "Viscosity of Liquids," p. 226, New York, 1929.
(2) Herschel and Bulkley, *Proc. Am. Soc. Testing Materials*, **26**, Pt. 2, 621 (1926).
(3) Karrer, Davies, and Dieterich, IND. ENG. CHEM., Anal. Ed., **2**, 96 (1930).
(4) Kraemers, *J. Rheology*, **1**, 76 (1929).
(5) Ostwald, *Kolloid-Z.*, **47**, 176 (1929).
(6) Smithsonian Tables, p. 156 (1921).

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Structural Changes during the Processing of Rubber[1]

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The effect of mastication, heating in air, oxygen, steam, and carbon dioxide gas, and the influence of light upon the plasticity of crude rubber have been investigated. Cold milling causes a permanent change in the consistency of crude rubber, whereas heating in air or steam produces a temporary effect. In absence of air the rubber exhibits a maximum amount of disaggregation at each given temperature. At low temperatures the increase in plasticity proceeds at practically the same rate whether the rubber is heated in oxygen or in carbon dioxide. Ultra-violet light affects concurrently both the plastic and elastic properties of the rubber.

The correlation between elasticity and double refraction of crude rubber has been shown. The anisotropic properties of rubber parallel the recovery values. In this investigation no agency has been found which causes such far-reaching and profound destruction of the elastic properties of the rubber as prolonged physical mastication.

The interrelation between plasticity and structure of crude rubber has been studied and the fundamental difference between actual mastication and heat breakdown has been emphasized. Prolonged milling, heating in air, or in oxygen destroy the protein framework of the rubber. Heating in steam or in an inert gas leaves it more or less intact.

Structural Nature of Crude Rubber

THE structure of the individual latex globule has been investigated in detail by Freundlich and Hauser (*5*), whose work, together with that of Sebrell, Park, and

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Martin (*25*), van Rossem (*23*), and others, indicates that ordinary crude unmasticated rubber is a very closely packed mass of discrete latex globules. De Vries (*29*) also assumes that during operations such as coagulation and drying in air the rubber globules remain intact. In recent excellent researches von Weimarn (*30*) has found that if rubber latex is treated with solvents or dispersing agents for proteins, such as lithium salts, the rubber will solidify during coagulation into a microscopically homogeneous coagulum.

Microscopical work described in a previous paper (*9*) indicated that crude, unbroken smoked sheet has its globular structure at least partly destroyed at the plantation during coagulation and sheeting. On mastication the rubber showed a gradual destruction of the globules, and finally, in dead-milled rubber a matrix was observed containing embedded small globules, which seemed capable of more resistance towards disintegration during milling than the larger ones. The proteins and natural resins meanwhile showed a gradual aggregation. The globular structure in acetone-extracted rubber had disappeared completely.

It is important, however, to differentiate distinctly between a globular structure and the fiber structure of rubber under stretch. The globular structure is associated with the secretion by the Hevea tree of pear-shaped and spherical rubber globules. These, to a greater or less degree, retain their identity in the crude rubber during processes following the coagulation. The fiber structure refers to the aggregation of the rubber hydrocarbon itself and is a logical interpretation of x-ray studies of rubber by Katz (*14*), Hauser and Mark (*11*), Clark (*3*), and others. Hoch and Siedler (*13*) have shown that it is possible to break up both cured and uncured rubber into fine fiber bundles by percussion of rubber that has been frozen in liquid air under stretch. Investigations on the double refraction of stretched rubber in polarized light by Zocher and von Fischer (*33*), Kroeger (*16*), van Geel and Eymers (*8*), and others also substantiate the conception of a fiber structure. Chemical work by Staudinger (*26*) on molecular chains of rubber, and by Pummerer and collaborators (*20*, *21*) on the isolation of two separate fractions of rubber hydrocarbon, have been further steps toward the interpretation of the elastic and plastic properties of the rubber hydrocarbon.

According to Bary and Hauser (*2*) rubber, on this basis, consists of a network of rubber hydrocarbon in a high state of aggregation and containing particles of a lower state of aggregation. Rubber, therefore, may be visualized as a jelly—i. e., as a system where the phases differ only as to their state of aggregation.

Theories as to Changes during Processing

The chief agencies which, after coagulation, affect the structure and consistency of crude rubber during processing are

mechanical work and heat. The effects of solvents and chemical agencies have not been considered in this investigation.

A number of theories are to be found in the literature explaining the gradual plastic change taking place in rubber during mastication. Pickles (*19*) points out that the flat portion of the plasticity curve begins at a point where the original cell structure has been broken down and represents the consistency of a homogeneous mixture of the various constituents of the rubber. Practically the same opinion is held by van Rossem (*24*). Garner (*7*) maintains that during the mastication of rubber globules are partially burst, and that depolymerized hydrocarbon is also formed. The tackiness is due to the action of oxygen and cannot appear until the latter is available. Klein and Stamberger (*15*), working with benzene solutions of crude masticated rubber, found that the number of ultra microscopical particles increased continuously with the milling. The original crude rubber formed a homogeneous suspension, whereas the completely milled rubber formed a heterogeneous suspension. This, they claim, indicates a breaking up of the protein framework during the milling.

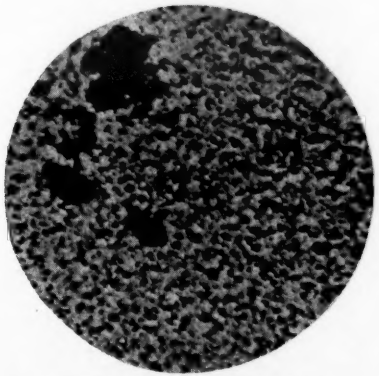
During mastication the rubber is influenced, not only by mechanical work, but also by heat, by oxygen of the air which becomes mixed with rubber, by light, etc. Temperatures below 100° C. seem to have only a slight effect upon rubber according to van Heurn (*12*) and de Vries (*28*). The effect of higher temperatures is more profound, especially in the presence of air. Staudinger and Geiger (*27*) found that the melting, or rather softening, point, where the rubber forms a soft mass, varies with impurities, with the mastication, with the time of heating, and with the presence or absence of oxygen. Fry and Porrit (*6*) claim that mechanical work, heat, and atmospheric oxygen are all responsible for the physical changes accompanying milling. At 150° C. the curve of viscosity against milling closely approximated the curve of viscosity against heating.

The plastic changes taking place when rubber is heated in air are without doubt to a great extent caused and regulated by the atmospheric oxygen. Van Rossem (*22*), studying the oxidation of rubber by heat, concluded that the oxidation was a secondary state preceded by depolymerization and that the depolymerization by heat is catalytically accelerated by oxygen. It is evident that there are two distinctly different effects produced by heat alone or by heat in combination with oxygen or with air.

In order to study the effect of heat alone, investigations have been made in which rubber was heated in steam or in an inert gas. Worthington and Hyde (*32*) heated rubber in an atmosphere of live steam free from air in order to produce a product of uniform softness. Park, Carson, and Sebrell (*18*) heated raw rubber at 158° C. for 24 hours. They show

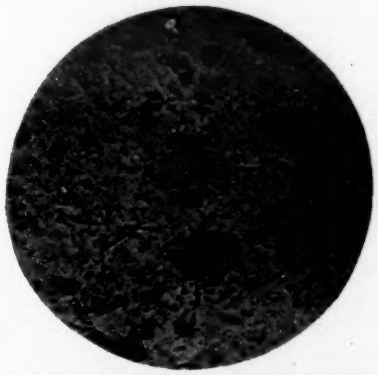
Micrograph 1—Unmasticated Rubber. 800 ×

$H_3 = 5.80$ $H_3 = 8.32$
$P = 34.5$ $Q = 0.364$



Micrograph 2—Rubber after 40 Minutes of Milling. 800 ×

$H_2 = 2.22$ $H_3 = 2.33$
$P = 82$ $Q = 0.010$



Micrograph 3—Rubber after 90 Minutes of Milling. 800 ×

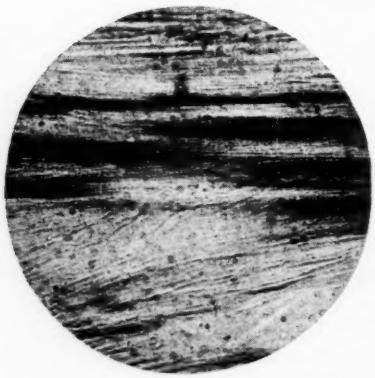
$H_2 = 1.43$ $H_3 = 1.46$
$P = 88.7$ $Q = 0.003$

an increase in plasticity corresponding approximately to five passes through a fairly tight mill.

Finally, the effect of light upon the structure and consistency of crude rubber should be mentioned. Garner (*7*) exposed masticated rubber to ultra-violet light and found that the action of this agent was partially aggregation and partially disaggregation, the extent of each being determined by the conditions prevailing. Previous to this, Asano (*1*) had demonstrated the formation of an insoluble modification of rubber by the action of ultra-violet light on pure rubber films in the absence of oxygen.

Experimental Procedure

PLASTICITY TESTS—The changes in plasticity of rubber taking place under the influence of various agencies were determined according to Williams (*31*). The method was selected in preference to viscosity determinations in order to obtain figures for both the flow and the recovery of the crude rubber. A modification of the Williams plastometer was used, supplied with roller guides to obtain a parallel movement of the upper platen in the press. The 2-cc. rubber pellet of cylindrical shape was preheated for 5 minutes at 100° C. The compressing force was 5000 grams. The test piece was placed in the press with the plates held apart by a small block of steel, and the readings were timed from the moment the steel block was withdrawn which let the weight fall on the sample. The original height of the rubber pellet, H_1, is a constant and equals 12.70 mm., corresponding to the edge of the steel block which keeps the plates apart. The flow number, H_2, is the height of the pellet in millimeters after 3 minutes of compression. The recovery value, H_3, is the height in millimeters 1 minute after the load is removed and the pellet has been allowed to recover under no load.



Micrograph 4—Unmasticated Rubber in Polarized Light at 300 Per Cent Stretch. 200 ×

H_2 = 5.80 H_3 = 8.32
P = 34.5 Q = 0.364

Micrograph 5—Rubber Milled for 90 Minutes in Polarized Light at 300 Per Cent Stretch. 200 ×

H_2 = 1.43 H_3 = 1.46
P = 88.7 Q = 0.003

The plasticity of the crude rubber was expressed in form of flow number H_2, recovery value H_3 and per cent permanent set, which equals $\frac{H_1 - H_3}{H_1}$. In order to obtain an expression embodying both flow and recovery of the rubber the following quotient was used: $\frac{H_3 - H_2}{H_1 - H_2}$. This quotient, which we will call Q in the following discussion, represents the ratio between flow and recovery in per cent and approaches zero the softer the rubber and approaches one the greater the elasticity. The expression should not be generalized and is used in this investigation for relative comparison of the effect of various agencies upon the plasticity of crude rubber. Per cent permanent set will be designated with P.

GLOBULAR STRUCTURE—For study of the globular structure of the rubber a modification of a previously described microscopical method was used (*9*), which was based on the lyophilic properties of the rubber proteins after treatment with water. In this manner the otherwise optically empty picture of crude rubber is changed into a microscopic field, in which distinct globules and aggregates of proteins can be observed. Thin sections of crude rubber ($0.5 \times 0.1 \times 0.01$ mm.) were boiled in water for 1 minute, the opaque rubber mounted in water and further compressed, and the edges of the cover glass sealed with paraffin. Photomicrographs of the slides were taken and the pictures obtained correlated with corresponding plasticity figures.

FIBER STRUCTURE—The double refraction of rubber at 300 per cent stretch was selected as a qualitative indication of the fiber structure and state of aggregation of the rubber hydrocarbon. Strips of crude rubber $10 \times 1 \times 1$ mm. were stretched 300 per cent crosswise over the slide and examined under crossed nicols in a polarizing microscope. The intensity of double refraction was noted and correlated with globular structure and plasticity figures. Photomicrographs were taken using a powerful arc lamp as a light source, light filters, and panchromatic plates.

PREPARATION OF RUBBER SAMPLES—A batch of 90 kg. of crude rubber obtained by blending selected parts of crude unmasticated smoked sheet was used for the experiments. The rubber was washed for 12 minutes on corrugated washing mills to remove impurities, dried, and homogenized for 6 minutes in a Banbury mixer. Thirty days were allowed to elapse before starting the various experiments to let the rubber assume constant conditions.

Mastication

Four thousand grams of rubber were broken down on a 20-inch (50.8-cm.) mill with cooling water on full at an average roll temperature of 56° C., and 200 grams of rubber were taken off every 5 minutes for examination. The broken-down rubber was allowed to recover for 24 hours in a constant-

temperature room at 21.1° C. and 65 per cent humidity, and the plasticity figures were determined. The plasticity determinations were repeated after 42 days of standing in constant temperature to establish the permanence of the changes in consistency brought about during milling. Table I shows the changes that crude rubber underwent when milled for 90 minutes under standard conditions. The flow numbers and recovery values represent the average of three determinations. Column I gives the figures 24 hours after milling and column II those after 42 days of standing.

Table I—Effect of Mastication on Plasticity of Rubber

Time of Milling	H_2		H_3		P		Q	
	I	II	I	II	I	II	I	II
Minutes								
0	5.80	..	8.32	..	34.5	..	0.364	..
5	4.26	3.97	4.85	4.62	61.8	63.5	0.070	0.074
10	3.57	3.35	3.93	3.66	69.0	71.2	0.039	0.033
20	2.92	2.90	3.16	3.12	75.1	75.0	0.025	0.022
30	2.51	2.45	2.65	2.54	79.1	79.8	0.014	0.009
40	2.22	2.34	2.33	2.40	82.0	80.8	0.010	0.006
60	1.78	1.88	1.84	1.94	85.6	84.6	0.006	0.005
80	1.65	1.56	1.68	1.56	87.0	87.6	0.003	0.000
90	1.43	1.56	1.46	1.56	88.7	87.6	0.003	0.000

The effect of mastication is expressed graphically in Chart 1. From the decrease of the quotient Q it can be seen that by far the greatest changes have taken place during the first 10 minutes of milling. The experiment also shows that cold mastication causes a permanent alteration of the consistency of the rubber. Practically the same results were obtained 24 hours after milling and after 42 days of standing. The immediate recovery which takes place during the first 8 hours after milling during hot storage according to Griffiths (*10*) has not been considered in this investigation, as the samples were given a rest period of 24 hours before the plasticity figures were determined.

Micrograph 1 shows the globular structure of unmasticated rubber. The rubber exhibits a very close network of globules, interspersed, however, with casual aggregates of proteins and resins. Progressive milling caused a loosening up of the protein framework, the individual constituents assumed more distinct contours, and a matrix was formed in connection with destruction and fusion of globules. After 40 minutes of breakdown (Micrograph 2) an optically empty matrix is observed as a background, in which individual globules are embedded in great number. The proteins and resins which in unmilled rubber form the border lines between the rubber globules are beginning to aggregate. After 90 minutes of milling (Micrograph 3) the globules have largely disappeared and only the very small ones remain. A homogeneous matrix has been formed in which, with exception of intact rubber globules, the aggregates of proteins and resins are distributed.

The unmasticated rubber showed an intense double refraction at 300 per cent stretch and the whole microscopical field was lighted up under crossed nicols. (Micrograph 4) Bright interference colors and indication of fiber alignment appeared parallel with the stretch. With progressive milling the double refraction decreased in intensity and ceased almost completely after 90 minutes. (Micrograph 5) The microscopical field remained practically dark and only the resin crystals lighted up the field. Of interest was the observation that the intensity of the double refraction fairly closely followed the recovery values of the rubber as obtained by plasticity determinations. The higher the recovery, the more intense was the double refraction. With destruction of the elastic properties of the rubber the anisotropic properties disappeared almost completely.

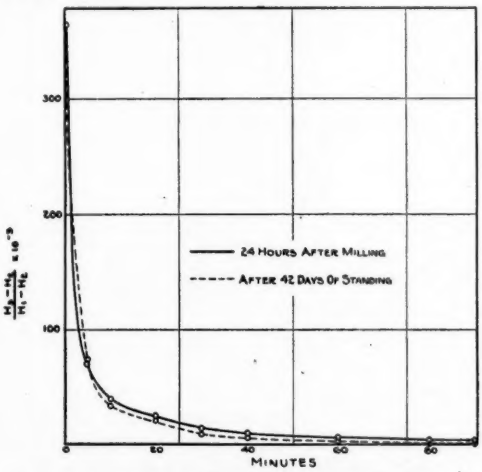


Chart 1—Effect of Mastication on Plasticity of Rubber

Heating in Air

The rubber was sheeted out to uniform thickness of 5 mm. on the 20-inch (50.8-cm.) mill, by means of three passes; 200-gram samples were heated in an electrical oven at 100° C. The plasticity figures were determined after 48 hours' recovery in a constant-temperature room, and the determinations repeated after 30 days of standing under constant conditions, to establish the permanency of changes observed. The changes taking place during increasing length of heating are presented in Table II. Column I gives the figures 48 hours after heating and column II those after 30 days of standing.

It can be seen that the heat chiefly influenced the recovery values of the rubber during the first hour of heating and that consequently a disaggregation of the rubber hydrocarbon took place. There were no indications of tackiness up to 150

minutes. During prolonged heating the disaggregation was followed by oxidation and after 18 hours the rubber was tacky and had lost its elasticity to a considerable extent. The globular structure and double refraction showed only slight changes during 150 minutes of heating.

In order to study the effect of heating at higher temperatures the experiment was repeated at 150° C. These results are also presented in Table II. After 60 minutes of heating the rubber appeared tacky, but still retained a considerable elasticity. A marked oxidation had taken place, which was first noticeable on the surface but which gradually spread through the whole rubber mass.

Table II—Effect of Heating in Air on Plasticity of Rubber

Time	H_2		H_3		P		Q	
	I	II	I	II	I	II	I	II
Minutes								
100° C.								
10	5.60	5.25	8.24	7.58	35.2	40.5	0.372	0.363
60	5.03	5.13	6.62	6.97	47.9	45.2	0.211	0.243
90	4.80	4.87	6.27	6.48	50.8	49.1	0.186	0.205
120	4.72	4.92	6.03	6.35	52.3	50.0	0.164	0.184
150	4.43	4.70	5.58	5.98	56.2	55.0	0.139	0.152
18 hours	2.78	3.00	3.01	3.18	76.0	75.0	0.023	0.018
150° C.								
10	5.43	5.37	7.95	7.53	41.2	40.7	0.346	0.294
30	4.68	4.65	5.91	5.85	53.3	54.0	0.162	0.146
60	2.73	3.03	2.92	3.51	76.9	72.1	0.019	0.050
90	2.65	2.67	2.75	2.94	78.2	76.9	0.010	0.027
120	2.47	2.56	2.56	2.80	80.6	78.0	0.009	0.024

Chart 2 shows the effect of heating in air at 100° and 150° C. upon the plasticity of the rubber. It can be seen that at 150° C. the changes proceed rather slowly up to about 60 minutes, as compared with mastication, while beyond this point the curve becomes fairly constant. Heating for 2 hours at 150° C. does not bring about so great a change in plasticity as 90 minutes of milling. The increase in plasticity probably is due partly to disaggregation of the rubber hydrocarbon, partly to oxidation, and partly to destruction of globular structure. There was a decided re-aggregation during 30 days of standing, contrary to the case with masticated rubber (*17*). The rubber also had become less tacky to the feel.

Micrograph 6 shows the globular structure of the rubber after hours of heating at 150° C. It can be seen that a destruction of globules has taken place, although it is less pronounced than that during prolonged mastication. A matrix has been formed probably owing to the bursting and fusion of globules.

Note—In a private communication Hauser has described unpublished observations on fusion of latex globules when heating protected liquid latex to 150–200° C. The globules assumed a spherical shape and the size increased up to 6–10 microns.

The globular structure showed only slight changes up to 30 minutes. A considerable aggregation of proteins and resins

took place during the heating in connection with bursting of globules, which checks with previous observations published in a study of the vulcanization process under the microscope (*9*).

The double refraction of crude rubber heated for 10 minutes

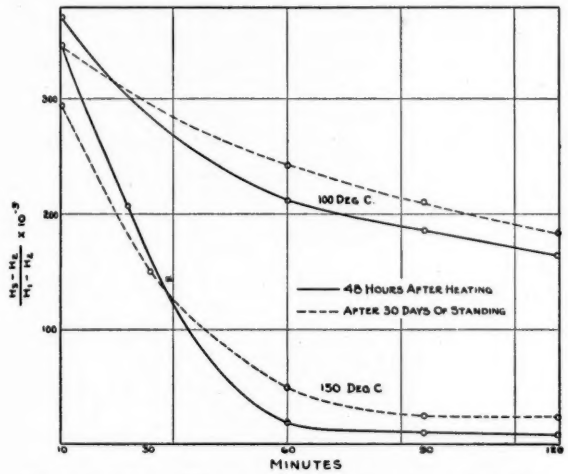


Chart 2—Effect of Heating in Air on Plasticity of Rubber

in air at 150° C. did not differ essentially from that of unheated rubber. After 2 hours of heating the anisotropic properties of the rubber were destroyed to a great extent and faint interference colors appeared in grayish blue under crossed nicols.

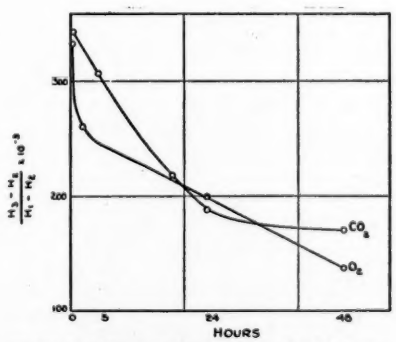


Chart 3—Effect of Heating in Oxygen and Carbon Dioxide on Plasticity of Rubber

Heating in Oxygen and in Carbon Dioxide

The rubber was sheeted out as in the previous experiment and heated in a Bierer-Davis oxygen bomb at a temperature of 70° C. and an oxygen pressure of 300 pounds per square

inch (21.09 kg. per sq. cm.). It would have been advisable to use the same temperature as in the previous experiment for a complete comparison, but the experimental possibilities were not at hand. Samples of rubber were heated for increasing lengths of time up to 72 hours. The experiment was repeated, replacing oxygen with carbon dioxide, to investigate to what extent the changes in plasticity were caused by oxidation and to what extent by heat, assuming that carbon dioxide would not affect the rubber. The results obtained are presented in Table III.

Table III—Effect of Heating in Oxygen and in Carbon Dioxide upon Plasticity of Rubber

Time	H_2		H_3		P		Q	
	O_2	CO_2	O_2	CO_2	O_2	CO_2	O_2	CO_2
Minutes								
30	5.33	5.27	7.78	7.82	38.8	38.5	0.333	0.343
60	5.13	....	7.54	....	40.6	....	0.318	.....
120	4.98	....	6.98	....	45.1	....	0.259	.....
300	....	5.15	....	7.47	....	41.3	.....	0.307
Hours								
18	....	4.72	....	6.46	....	49.3	.....	0.218
24	4.77	4.50	6.35	6.03	50.0	52.5	0.199	0.187
48	4.50	4.45	5.55	5.87	56.2	53.9	0.138	0.171
72	3.95	....	4.72	....	62.8	....	0.078	.....

Chart 3 shows the effect upon plasticity of heating rubber at 70° C. in oxygen and carbon dioxide. The decrease in elastic properties after 24 hours of heating was practically the same in oxygen and carbon dioxide. There was a more rapid initial decrease in case of oxygen. After 24 hours of heating the carbon dioxide curve became fairly constant, whereas the elastic properties continued to decrease when heating in oxygen.

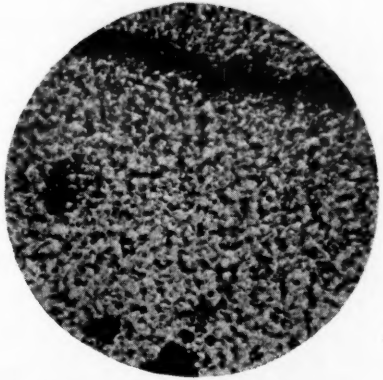
Micrograph 7 shows the effect of oxygen on the globular structure of the rubber. There were practically no changes up to 1 hour of heating. After longer periods of heating a destruction of globules was noted which was accompanied by aggregation of proteins and resins. The globules were retained almost completely in carbon dioxide during the whole period of heating. (Micrograph 8) The interference colors faded both in oxygen and in carbon dioxide.

Heating in Steam

Two hundred gram samples of 5 mm. thick sheets were heated in a pot press in live steam at 54 pounds per square inch (3.796 kg. per sq. cm.) corresponding to a temperature of 150° C. Steam was blown through the pot press five times after raising the pressure to 54 pounds each time to assure that no air remained. The pot was allowed to cool for 10 minutes before being opened and the rubber immediately after being taken out was immersed in cold water to prevent air oxidation. During the steam treatment the rubber absorbed approximately 10 per cent of water and showed a milky white color.

Micrograph 6—Rubber Heated in Air for 2 Hours at 150° C. 800 ×

H_2 = 2.47 H_3 = 2.56
P = 80.6 Q = 0.009



Micrograph 7—Rubber Heated in Oxygen for 72 Hours at 70° C. 800 ×

H_2 = 3.95 H_3 = 4.72
P = 62.8 Q = 0.078

Micrograph 8—Rubber Heated in Carbon Dioxide for 48 Hours at 70° C. 800 ×

H_2 = 4.45 H_3 = 5.87
P = 53.9 Q = 0.171

The water was removed by drying the sheets in an electric oven at 55° C. with circulating air until complete transparency was attained. The rubber recovered somewhat and lost its pliability during drying. The plasticity figures were determined 48 hours after heating and after 30 days of standing in a constant-temperature room at 21.1° C. and 65 per cent humidity. (Table IV)

Table IV—Effect of Heating in Steam on Plasticity of Rubber

Time	H_2		H_3		P		Q	
	I	II	I	II	I	II	I	II
54 lbs. (3.8 kg.)								
Minutes								
15	4.57	4.50	5.70	5.33	55.2	58.0	0.139	0.102
30	4.26	4.30	5.16	5.08	59.4	60.0	0.106	0.092
60	4.15	4.15	4.82	4.92	62.0	61.3	0.078	0.090
120	3.85	4.02	4.43	4.76	65.0	62.5	0.065	0.086
360	3.75	4.00	4.22	4.76	66.8	63.0	0.053	0.085
Hours								
24	3.60	3.97	4.06	4.67	68.0	63.3	0.051	0.080
48	3.41	3.83	3.89	4.48	69.5	64.8	0.052	0.073
72	3.35	3.70	3.82	4.34	70.0	66.0	0.050	0.071
85 lbs. (6 kg.)								
Minutes								
0	5.83	....	8.40	....	33.9	....	0.375	.....
15	4.73	4.57	6.00	6.22	52.9	51.0	0.160	0.202
30	4.60	4.47	5.71	5.79	54.9	60.0	0.137	0.160
60	4.12	4.10	4.88	4.95	61.7	61.0	0.089	0.099
360	3.58	3.75	3.99	4.43	68.5	65.1	0.045	0.076
Hours								
24	3.35	3.63	3.81	4.16	69.9	67.3	0.049	0.059
48	3.23	3.57	3.60	4.09	71.5	68.0	0.039	0.057
72	3.02	3.40	3.30	3.91	74.0	69.0	0.029	0.055

The increase in plasticity when heating in steam at 150° C. is considerably less than when heating in air at the same temperature. A marked recovery of the rubber took place during 30 days of standing.

In order to obtain maximum breakdown with the equipment at hand, the experiment was repeated at 85 pounds pressure (5.976 kg. per sq. cm.) corresponding to 164° C. The rubber was allowed to dry at a constant temperature of 21.2° C. and 65 per cent humidity. The sheets did not become transparent until after 1 week of drying. The plasticity figures were determined 10 days after heating and the determination repeated after 48 additional days of standing. The results are presented in Table IV.

The effect of steam treatment is shown graphically in Chart 4. A considerable increase in plasticity took place, the main changes occurring during the first 6 hours of heating. It was not possible to break down the rubber more than to a certain degree, which probably corresponds to maximum disaggregation at the temperatures used. This is indicated in the almost horizontal part of the curves proceeding from 6 to 72 hours. Contrary to the case with masticated rubber, the steam treatment causes a more or less temporary effect and the rubber recovers some of its elasticity during standing.

The recovery during standing is the more marked the less the rubber is broken down when the steam treatment commences. Unbroken smoked sheet, heated for periods up to 24 hours at 164° C., showed a considerably greater recovery during standing than rubber that had had a preliminary breakdown on a mill prior to the steam treatment. On the other hand, the increase in plasticity during heating in steam became less the more the rubber was masticated before heating. The slight increase in plasticity was evidently due to the originally low recovery values, which indicated that only a limited amount of aggregated rubber was at hand and that consequently a very slight disaggregation could be expected. The higher the recovery values the greater will be the thermal disaggregation of the rubber hydrocarbon during steam treatment.

During the process of heating in steam the rubber globules and proteins absorb water and swell considerably. Samples for microscopical examination were taken after drying the rubber to transparency and slides were prepared in the usual manner. Micrograph 9 shows the globular structure after 24 hours of heating. The rubber retains the protein framework almost completely.

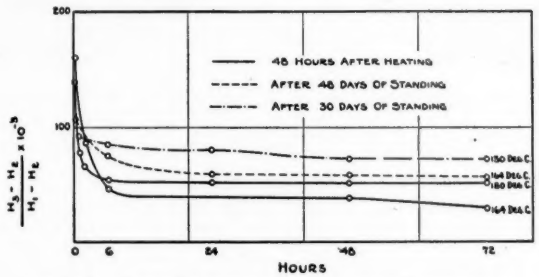


Chart 4—Effect of Heating in Steam on Plasticity of Rubber

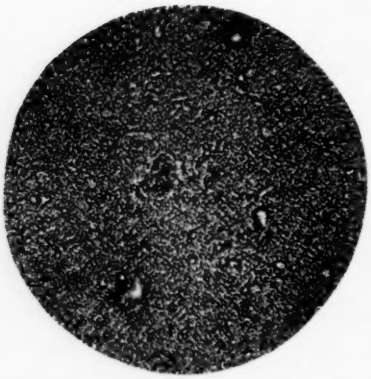
The anisotropic properties of the rubber after 72 hours' heating in steam were much more pronounced than those after heating in air for 2 hours at 150° C.

The experiment shows that the increase in plasticity is chiefly caused by disaggregation of the rubber hydrocarbon itself. It is possible to increase the plasticity of crude, unmasticated smoked sheet to a certain limit by steam treatment, but it is not possible to obtain completely broken down rubber. To achieve this it is necessary to destroy also the globular structure, which remains more or less intact during the steam treatment, at least at the temperatures used.

Effect of Light

The rubber was sheeted out to 5 mm. thickness and exposed for increasing lengths of time to a mercury quartz lamp at an average temperature of 43° C. and at a distance from the lamp of 26.67 cm. Only one side of the rubber was exposed. Samples for plasticity determination were prepared by press-

ing the rubber between holland by hydraulic pressure of 150 pounds per square inch (10.55 kg. per sq. cm.) at 80° C. for 2 minutes (*4*). The experiment was repeated exposing the rubber to a carbon arc lamp, the spectrum of which closely approximated sunlight and the intensity corresponded to the bright sunlight of a day in June. The temperature during the exposure varied from 35° to 38° C. and the rubber was placed at 20.42 cm. from the lamp. The results of the plasticity determinations are presented in Table V.



Micrograph 9—Rubber Heated in Steam for 24 Hours at 164° C. 800 ×

H_2 = 3.35 H_3 = 3.81
P = 69.9 Q = 0.049

Micrograph 10—Rubber Exposed to Ultra-Violet Light for 5 Hours at 43° C. 800 ×

H_2 = 5.18 H_3 = 7.33
P = 42.4 Q = 0.285

Table V—Effect of Light on the Plasticity of Rubber

Time	H_2		H_3		P		Q	
	M-Q	C-A	M-Q	C-A	M-Q	C-A	M-Q	C-A
Minutes								
0	5.80	....	8.32	....	34.5	....	0.364	.....
15	5.50	....	8.50	....	33.1	....	0.417	.....
30	5.38	5.58	8.28	8.15	34.8	35.8	0.395	0.360
60	5.23	5.63	7.97	8.49	37.3	33.2	0.367	0.405
120	5.18	5.75	7.88	8.44	37.9	33.6	0.359	0.387
300	5.18	5.42	7.33	8.20	42.4	35.4	0.285	0.383

During the exposure the surface of the rubber became hard and dry, indicating aggregation. After longer periods of exposure, however, the rubber became decidedly softer, especially in ultra-violet light. Chart 5 shows the effect of the exposure on the plasticity of the rubber. The flow numbers decrease concurrently with an increase of recovery values, resulting in a curve with a peak, indicating both aggregation and disaggregation of the rubber hydrocarbon.

Micrograph 10 shows the globular structure after 5 hours' exposure to ultra-violet light. Only slight changes were noted and the double refraction did not differ essentially from that of unexposed rubber.

Discussion

Plasticity values of crude rubber based on flow and recovery are probably chiefly regulated by the state of aggregation of the rubber hydrocarbon and the degree of breakdown, fusion, or bursting of rubber globules. The first factor presumably is of the greatest importance. Cold breakdown embodies an

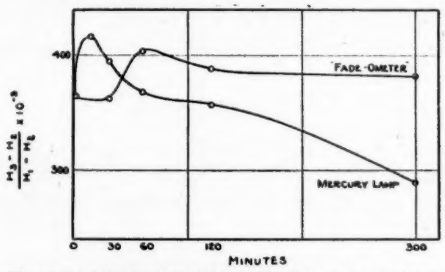


Chart 5—Effect of Light on Plasticity of Rubber

actual destruction and fusion of globules, and the hydrocarbon at the same time disaggregates. The result is permanent softness. Heating rubber in air causes a partial destruction and fusion of globules in combination with thermal disaggregation and oxidation. It seems that oxygen is needed for breaking up and fusion of globules, at least at the temperature

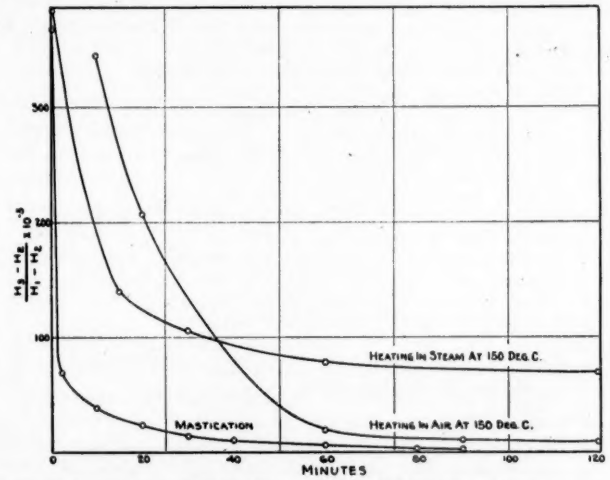


Chart 6—Effect of Mastication and Heating in Air and Steam on Plasticity of Rubber—Summary

used in this investigation. When heating rubber in steam the globular structure is retained almost completely and the increase in plasticity is due to thermal disaggregation of the rubber hydrocarbon, which is followed by re-aggregation during standing of the rubber. In absence of air the rubber exhibits a maximum amount of disaggregation at each given tempera-

ture. The plastic changes are more or less reversible as long as the globular structure of the rubber remains intact.

The effect of mastication and heating in air and in steam are expressed graphically in Chart 6. The curves show that the plasticity becomes fairly constant after 15 minutes of milling, whereas corresponding figures for heating in air and in steam are about 1 hour. In this investigation no agency has been found which causes such far-reaching and profound destruction of the elastic properties of the rubber as prolonged physical mastication.

Acknowledgment

The author wishes to express his thanks to O. M. Hayden, of E. I. du Pont de Nemours and Company, who has had the kindness to have the irradiation experiments conducted in his laboratories.

Literature Cited

(1) Asano, *India Rubber J.*, **70**, 307, 347, 389 (1925).
(2) Bary and Hauser, *Kautschuk*, **4**, 96 (1928); see also Ariano, *India Rubber J.*, **78**, 316 (1929).
(3) Clark, IND. ENG. CHEM., **18**, 1131 (1926).
(4) Cranor, *Ibid.*, **17**, 1202 (1925).
(5) Freundlich and Hauser, *Kolloid-Z.*, Spec. No., **36** (1925).
(6) Fry and Porrit, *Trans. Inst. Rubber Ind.*, **3**, 203 (1927).
(7) Garner, *Ibid.*, **5**, 413 (1929).
(8) Geel, van, and Eymers, *Z. physik. Chem.*, **3**, 240 (1929).
(9) Grenquist, IND. ENG. CHEM., **21**, 665 (1929); see also Hauser, *Kautschuk*, **5**, 151 (1929).
(10) Griffiths, *Trans. Inst. Rubber Ind.*, **1**, 308 (1926).
(11) Hauser and Mark, *Kolloidchem. Beihefte*, **22**, 60 (1926).
(12) Heurn, van, Delft. Comm., Pt. 4, p. 116.
(13) Hoch and Siedler, *Kautschuk*, **1**, 10 (October, 1925).
(14) Katz, *Chem.-Ztg.*, **49**, 353 (1925).
(15) Klein and Stamberger, *Kolloid-Z.*, **35**, 362 (1924).
(16) Kroeger, *Ibid.*, **45**, 52 (1928).
(17) Marzetti, *Giorn. chim. ind. applicata*, **6**, 567 (1924).
(18) Park, Carson, and Sebrell, IND. ENG. CHEM., **20**, 478 (1928).
(19) Pickles, *Trans. Inst. Rubber Ind.*, **1**, 96 (1925).
(20) Pummerer and Gundel, *Ber.*, **60B**, 1583 (1928).
(21) Pummerer and Miedel, *Ibid.*, **60B**, 2148 (1927).
(22) Rossem, van, *Caoutchouc & gutta-percha*, **10**, 6961 (1913).
(23) Rossem, van, *Chem. Weekblad*, **20**, 9 (1923).
(24) Rossem, van, *Trans. Inst. Rubber Ind.*, **1**, 73 (1925).
(25) Sebrell, Park, and Martin, IND. ENG. CHEM., **17**, 1173 (1925).
(26) Staudinger, *Ber.*, **62**, 2893 (1929).
(27) Staudinger and Geiger, *Helv. Chim. Acta*, **9**, 549 (1926).
(28) Vries, de, "Estate Rubber," p. 277.
(29) Vries, de, *Trans. Inst. Rubber Ind.*, **3**, 284 (1927); see also De Vries and Beumée-Nieuwland, *Mededeel. Proefsta. Rubber*, **13**, No. 43 (1929); Beumée-Nieuwland, *Ibid.*, **13**, No. 44 (1929).
(30) Weimarn, v., *Bull. Chem. Soc. Japan*, **3**, 157 (1928).
(31) Williams, IND. ENG. CHEM., **16**, 362 (1924).
(32) Worthington and Hyde, U. S. Patent 1,360,485 (November 30, 1921).
(33) Zocher and von Fischer, *Kautschuk*, **5**, 173 (1929).

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Carbon Black in Rubber Insulating Compounds[1]

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Up to about 10 per cent by weight of properly made and dried carbon black may be added to each 100 parts of rubber hydrocarbon present in rubber insulating compounds with marked improvement in dielectric strength, resistivity, and power factor, and without serious increase in dielectric constant.

The exact amount of carbon black required depends somewhat on which electrical property is to be brought to its maximum value. Fresh, uncompounded carbon black must be employed.

Electrical improvements of up to 50 per cent are possible.

The improvement is thought to be due to the removal by the carbon black of the ultimate traces of moisture and electrolytic impurities.

PART I—THEORETICAL

RUBBER is a non-conductor or dielectric. Carbon black consists mostly of carbon, which is a conductor and so not a dielectric. Therefore, the addition of the latter to the former must detract from its dielectric properties. Thus current belief, and thus the literature.

The contrary is the case. The admixture in suitable proportions of carbon black to rubber insulating compounds not only does not injure but may improve them, and to a striking extent.

Dielectric Properties of Rubber

CRUDE RUBBER—Crude rubber is an excellent insulator,

[1] Received April 15, 1930. Presented before the Division of Rubber Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

the resistivity being of the order of 5000×10^6 megohms per cc. (1968×10^6 megohms per cu. in.). The power factor is of the order, 0.2. The dielectric constant, at 1000 cycles, is of the order, 2.5 (*10*).

Note—Power factor, as applied to a dielectric, measures its tendency to dissipate electrical energy when subjected to alternating voltage. It is usually expressed as a percentage. Thus the "power factor" is the electrical analog of friction in a machine.

PURE VULCANIZED RUBBER—With pure-gum mixes of rubber and sulfur the resistivity ranges irregularly from 1000×10^6 to $15{,}000 \times 10^6$ megohms per cc. (*11*) (394×10^6 to 591×10^6 megohms per cu. in.). The power factor at given frequency is a function of the sulfur ratio reaching 9 per cent (*12*). The dielectric constant also ranges irregularly from 2.6 to nearly 5, depending on frequency (*12*).

COMPOUNDED RUBBER—Most types of inorganic compounding ingredients are stated to behave as follows:

As regards resistivity, there is no great change when added in moderate amounts (*4*). As regards power factor, most fillers increase it (*5*).

Regarding dielectric constant, we are told that fillers increase this value, the "extent depending on the amount used and the characteristics of the filler" (*6*). The effect of carbon black as a compounding ingredient is stated to be different from that of other fillers, owing to its being a conductor. As little as 0.2 per cent is stated to have a perceptible effect, whereas "with 20 per cent, the dielectric constant is more than double that of the base compound. The increase in dielectric constant is almost linear and is much greater than with equal amounts of other fillers."

Thus, for example, we read (*7*):

The introduction of carbon greatly decreases the resistivity of rubber. This effect is not apparent, however, with 0.2 to 2 per cent of carbon. With 10 per cent carbon some of the specimens show a resistivity of 2000×10^6 M. O. per cc. which is not lower than that of some pure rubber compounds. With higher percentages of carbon, however, the resistivity falls off with greater rapidity.

As to power factor, it is stated that "with 10 per cent of carbon black the power factor is about ten times that of the base compound, and with 20 per cent it is nearly 30 times that of the base compound."

EFFECT OF MOISTURE—Moisture is injurious because of its power to dissolve and ionize any traces of electrolytes, on the one hand, and of its own effect, on the other.

For details as to its effect on the dielectric constant, resistivity, and power factor, the reader may consult Boggs and Blake (*2*), Williams and Kemp (*19*), and Nuttall (*14*). In brief, moisture profoundly affects all of these electrical properties, not only in the case of rubber, but also in the case of insulating oils, where 1 part in 10,000 reduces the breakdown voltage by 70 per cent (*14*). The view has even

been advanced that the "insulation resistance of an insulating material is really a measure of its degree of dryness."

Properties of Carbon Black

COMPOSITION—The composition of carbon black varies according to the method of manufacture. For example, a "roller" black as manufactured for the ink trade will analyze about 91 per cent of carbon, the remainder consisting essentially of oxygen (*3*). Carbon black made on channels as furnished to the rubber industry will analyze about 96.7 per cent of carbon, together with oxygen, hydrogen, etc. In addition to these non-carbonaceous elements, carbon black of course contains a relatively large amount of entrained air, which, however, is practically all eliminated during admixture into rubber. Owing to its extremely small size—*ca.* 80 millimicrons (mμ)—the exact structure and relationship of the carbon to the non-carbon components are not known. In any case it cannot, a priori, be assumed that the

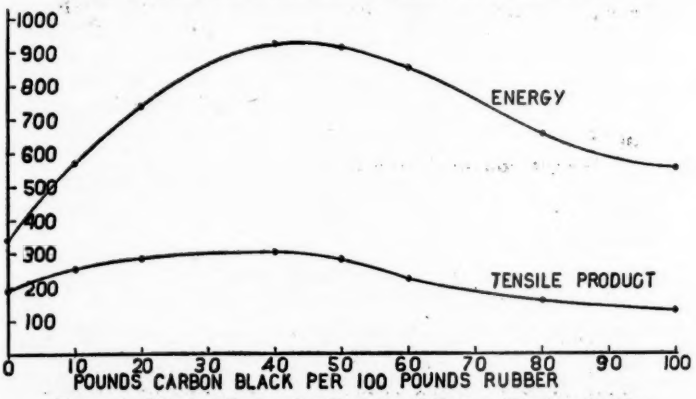

Figure 1—Effect of Increasing Dosages of Carbon Black in Rubber

electrical behavior of carbon black, when dispersed in rubber or in any other medium, will be that expected of a pure carbon phase.

Table I—Adsorption Properties of Carbon Black

Black	Gain in Weight after Long Exposure over Water	DPG Adsorption Index	KOH Adsorption Index
	%	%	%
"Rubber" grade	4	10	20
Special No. 1	30	40	47
Special No. 2	56	88	82

STRUCTURE WHEN DISPERSED IN RUBBER—Despite several serious efforts to study the morphology of carbon black dispersions in rubber by means of the microscope (*9*), it is not known how completely carbon black is dispersed nor how its particles "pile" or arrange themselves.

By indirect reasoning, however, we may be certain that with increasing concentration agglomeration sets in (*18*).

The curves in Figure 1 illustrate the decay in physical properties as the percentage of carbon black is increased beyond a certain point (*1*).

Note—The onset of agglomeration is also clearly indicated by heat of wetting experiments. See the excellent studies of Hartner, *Kolloid-chem. Beihefte*, **30**, 83 (1929).

At very high concentrations there would appear to be a partial inversion of phase in which some rubber units are surrounded by carbon black instead of the carbon-black particles being surrounded by rubber. This results in a leather-like structure which, curiously enough, is already the basis of an important division of the rubber industry. At the lower concentrations the dispersion of carbon black becomes relatively complete.

ADSORPTION BEHAVIOR—Like other forms of active carbon, carbon black may show a strong avidity for moisture and for dissolved substances.

Table I shows, merely by way of illustration, the "removal" effect of different types of carbon black on water, on an alcoholic solution of diphenylguanidine, and on an aqueous solution of potassium hydroxide (these solutions being approximately 0.01 normal in strength). The details of carbon black "removal" will be discussed in a later communication. It is mentioned at this time to explain the reasoning which led up to the experiments of this paper.

We pass now to a consideration of the known facts about other conducting materials when in a state of colloidal dispersion in dielectrics.

Electrical Properties of Conducting Substances Colloidally Dispersed in Dielectrics

Smoluchowski (*15*) has calculated the conductivity to be expected in a pure sol of gold, for example, and arrives at a figure of 1.2×10^{-7}, an extremely low value. It would appear that the conductivity of dilute metallic sols is influenced very little by the conductivity of the dispersed metallic particles.

Svedberg (*16*) states:

"In some cases the conductivity of the sol has been found to be even less than the conductivity of the dispersion medium. If we disperse mercury in pure conductivity water by means of the oscillatory arc, the conductivity decreases. That probably is due to the adsorption on the mercury particles formed of the impurities present. The conductivity, therefore, decreases. The small contribution to conductivity from the particles can, of course, be disregarded."

The work of Whitney and Blake (*17*) and of Nordenson (*13*) indicates that with most metallic sols the small conductivity observed arises from residual electrolytes (remaining as impurities on the dispersed phase).

In view of the foregoing it seemed unnecessary to assume that a conductor such as carbon black should prove any more deleterious when dispersed in low percentages in rubber

than does gold, a much better conductor, when dispersed in water.

Furthermore, the injurious action of water, and of water-soluble impurities, taken in conjunction with the well-known adsorptive activity of carbon black toward water (and such dissolved substances) suggested that the addition of carbon black in the proper amount might not only leave the dielectric properties of rubber intact but even improve them. In other words, it was hoped that the improvement due to the possible removal (the word "removal" is here used in the electrical sense) of these impurities, might be attained before being overtaken by the ill effects associated with the higher concentrations of carbon black.

PART II—EXPERIMENTAL

The following experiments on carbon black insulating compounds were carried out in the laboratories of the Simplex Wire and Cable Co., Boston, Mass.

Experimental Conditions

The crude rubber used was smoked sheets broken down 30 minutes in a full-size internal mixer, washed, and vacuum-dried in the factory. Zinc oxide (Red Seal) and whiting were dried to constant weight at 212° F. (100° C.). The carbon black (Micronex) was heated 2 hours at 325° F. (166° C.).

The compounds were mixed on a small laboratory mill, great care being taken to insure uniform dispersion of the mineral ingredients. The dried powders were carried direct from the oven to the mill. After mixing, the compounds were stored 24 hours in a closed vessel containing calcium chloride.

The samples were cured in a laboratory hydraulic platen press, the temperature being 270° ± 0.5° F. (132° C.). Preliminary cures were carried out on the base compound and on the compounds containing the minimum and maximum percentages of carbon black. From these results the best technical cure was determined as 30 minutes, which was the cure used for all samples. The samples were tested at 73° F. (23° C.).

Electrical Tests—Embedded aluminum electrodes were used in all tests except break-down, and carefully centered on the uncured sample prior to vulcanization. An electrode, of 6-inch (15.24-cm.) diameter, was placed over, and a $6^1/_2$-inch (16.5-cm.) electrode on the bottom of, each sample. The samples were approximately $9^1/_4$ inches (24.4 cm.) square, the thickness averaging 0.060 inch (0.15 cm.) between electrodes. Triplicate samples were tested for each cure. The voltage (break-down) results were obtained on the same samples, employing 2-inch (5.08-cm.) disks.

The 1000-cycle dielectric constant was obtained by means of a General Radio capacitance bridge, using a tuning fork oscillator as the source of power. The 1000-cycle power

factor was obtained simultaneously with the capacity (to which the dielectric constant is directly proportional), and was calculated from the circuit values, when balance was obtained.

The d. c. dielectric constant was calculated from the dimensions of the sample and the capacity obtained by comparing the deflection of a ballistic galvanometer when the sample was discharged through it immediately after a 10-second charge at 300 volts, with the standard deflection obtained from a standard condenser under similar conditions.

The resistivity was measured by the loss-of-charge method. The sample was charged at 300 volts for 10 seconds, disconnected from the charging battery and, after standing 1 minute, discharged through the ballistic galvanometer. The

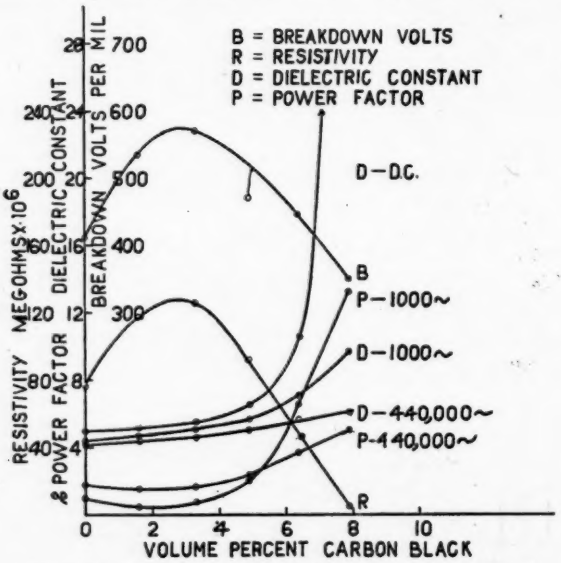

Figure 2—Effect of Carbon Black in 40 Per Cent Rubber Insulating Compound

resistivity was calculated from the capacity and the ratio of the deflection due to the delayed discharge to that obtained by discharge immediately after the charging battery was disconnected.

Dielectric-strength tests were made by using 2-inch (5.08-cm.) round disks, the voltage being raised at the rate of 1000 volts per second.

Reduction of Data

In view of the experimental difficulties in obtaining close duplicates in the electrical measurements, arithmetic means were used, first rejecting wild values. The "four-times" rule was used to determine "wildness." That is, the mean of the two closest values was computed. Their average devia-

tion and the deviation of the remaining value from the above mean compared with this average deviation. Any value showing a deviation four or more times the average deviation was rejected.

40 PER CENT RUBBER COMPOUND

Smoked sheets	40.45
Whiting	42.10
Zinc oxide	13.30
Paraffin	2.21
Agerite powder	0.22
Monex	0.12
Sulfur	1.60
	100.00

Carbon black (Micronex) was used in the above compound to replace whiting by progressive volume substitution.

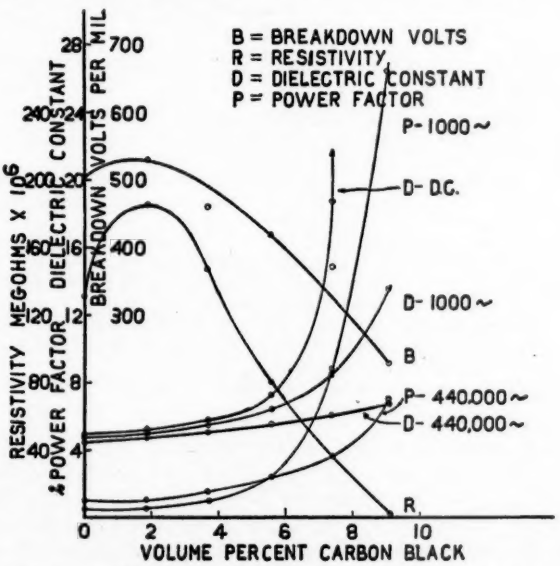

Figure 3—Effect of Carbon Black in 30 Per Cent Rubber Insulating Compound

The results are shown graphically in Figure 2. These data may be summarized as follows:

(1) At approximately $3^1/_4$ per cent of carbon black (Micronex) by volume or 4 per cent by weight, the breakdown voltage was raised from 408 to 571, an increase of 40 per cent.

(2) The resistivity was raised from 76×10^6 megohms per cubic inch to 128×10^6 megohms per cubic inch (193×10^6 M. O. per cc. to 325×10^6 M. O. per cc.), an increase of 68 per cent.

(3) The dielectric constant was changed for d. c. from 4.94 to 5.34; at 1000 cycles from 4.39 to 4.99; at 440,000 cycles from 4.26 to 4.67. It is seen that the specific inductive capacity has not been materially raised by this addition of carbon black.

(4) At 1000 cycles the power factor has decreased from 1.05 to 0.793, an improvement of 24 per cent. (With 2 per cent by volume of carbon black (Micronex) the power factor was

only 0.541, a decrease of 48 per cent.) At 440,000 cycles the power factor dropped from 1.81 to 1.46, a decrease of 19 per cent.

It will be noted that, with no significant raising of the dielectric constant, the addition of 4 per cent (10 per cent on the crude rubber) of carbon black—a conductor—has improved the dielectric strength, resistivity, and power factor of a typical high-quality insulating compound by about one-half.

30 PER CENT RUBBER COMPOUND

Smoked sheets	30.17
Whiting	53.29
Zinc oxide	11.16
Litharge	2.48
Ozokerite	1.24
Agerite powder	0.15
Monex	0.12
Sulfur	1.39
	100.00

Carbon black again replaced whiting in equivalent volume increments.

The tests on this compound are shown graphically in Figure 3. The results may be summarized as follows:

(1) At approximately 2 per cent by volume (slightly more by weight) breakdown increased from 505 volts per mil to 528 volts per mil, an increase of 5 per cent.

(2) Resistivity increased from 131×10^6 M. O. per cubic inch to 186×10^6 M. O. per cubic inch (333×10^6 M. O. per cc. to 473×10^6 M. O. per cc.), an increase of 42 per cent.

(3) Dielectric constant (d. c.) increased from 4.83 to 5.20; at 1000 cycles from 4.66 to 5.02; at 440,000 cycles from 4.37 to 4.70. Here again it will be noted that there is no significant increase in the dielectric constant.

(4) The power factor at 1000 cycles increased from 0.57 to 0.59; substantially no change.

Here again we note a definite electrical improvement in the case of the lower quality (30 per cent) compound, the effect being less than with the 40 per cent compound. This suggests that the beneficial effect of the added carbon black may be due to the removal of certain impurities which are associated with the crude rubber present in the compound.

35 PER CENT COMPOUND CONTAINING RECLAIMED

Smoked sheets	35.5
Alkali reclaimed tires[a]	21.7
Zinc oxide	23.0
Mineral rubber	17.3
Agerite powder	0.5
Accelerator	0.1
Sulfur	1.9
	100.0

[a] The reclaimed rubber contained the carbon black originally present in the tire treads. This carbon black is not shown in the data, since it is not "fresh," having passed through the reclaiming process.

In this case both the reclaimed rubber and the crude rubber were vacuum-dried to constant weight. Zinc oxide was replaced by carbon black (Micronex) in progressive volume for volume substitutions.

The results are shown in Figure 4, and may be summarized as follows:

(1) At approximately 3 per cent by volume (5 per cent by weight) of carbon black breakdown in volts per mil increased from 370 to 420, an increase of 14 per cent.

(2) Resistivity at approximately 1 per cent by volume (1.5 per cent by weight) increased from 627 × 10^6 M. O. per cubic inch to 643 × 10^6 (1590 × 10^6 M. O. per cc. to 1635 × 10^6 M. O. per cc.), an increase of 2.5 per cent.

(3) Dielectric constant increased from 4.27 to 4.35, an increase of 1.9 per cent. At 1000 cycles it increased from 3.94 to 4.02, an increase of 2.1 per cent.

(4) At 2 per cent carbon black by volume (3 per cent by weight) the power factor was improved from 1.25 to 1.12, a decrease of 10 per cent.

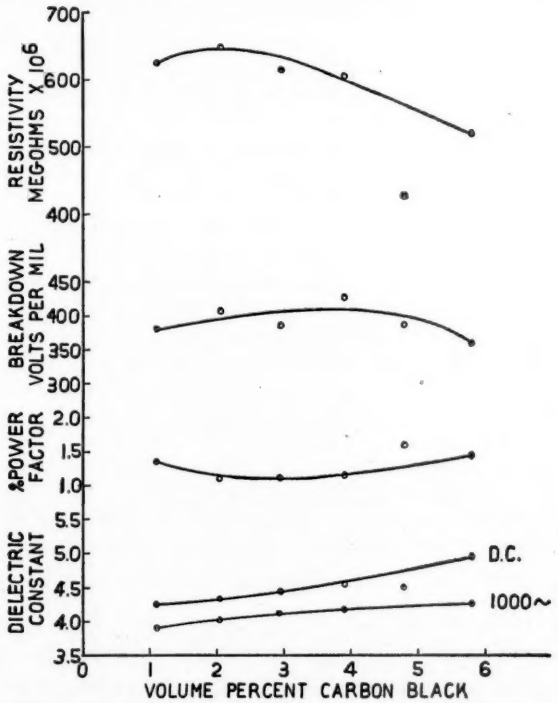

Figure 4—35 Per Cent Compound Containing Reclaimed

Here again there has been definite improvement in electrical properties without important change in dielectric constant.

Conclusions

1—It has been shown that, in conformity with published behavior of other conducting substances (metallic sols, etc.), carbon black may be incorporated in a dielectric such as rubber without detracting from its insulating or dielectric properties. Published results to the contrary were in error,

probably because the material was added in excessive amounts.

2—In addition to this effect, it has been shown that the well-known ability of carbon black to adsorb water and dissolved electrolytes endows carbon black–rubber insulating compounds of various types with improved dielectric strength, resistivity, and power factor, the specific inductive capacity remaining substantially unchanged. In some cases this improvement may exceed 50 per cent.

3—The prevailing opinion that carbon black is injurious to rubber insulating compounds which are to be used next to the wire, or which in general are expected to serve as electrical insulation, has been shown to be erroneous, provided the proper proportions are employed.

4—These results would seem to render advisable the rewriting of many specifications dealing with rubber insulating compounds, and thus make it possible to apply the well-known beneficial effects of carbon black compounding—improved toughness, density, wearing resistance, imperviousness to light, tear resistance, etc.—to the electrical insulation field, from which it has hitherto been barred.

5—Although it is strongly recommended that the proper dosage of carbon black (which must be of suitable quality and thoroughly dry) be redetermined in each case, the writers' results would indicate that up to 10 per cent of carbon black on the crude rubber (plus the rubber content of any reclaimed rubber present) will effect the desired improvement in electrical properties.

Acknowledgment

The writers desire to express their thanks for aid in preparation of the data to E. M. Follansbee and W. N. Eddy, of the Simplex Wire & Cable Company, and to J. W. Snyder, of Binney & Smith Company.

Literature Cited

(1) Binney & Smith Laboratories, Unpublished results.
(2) Boggs and Blake, IND. ENG. CHEM., **18**, 224 (1926).
(3) Bur. Mines, *Bull.* **192**, p. 73.
(4) Curtis and McPherson, Bur. Standards, *Tech. Paper* 299, p. 722.
(5) *Ibid.*, p. 721.
(6) *Ibid.*, p. 720.
(7) *Ibid.*, p. 713.
(8) Green, "Microscopy of Paint and Rubber Pigments" (1922.)
(9) Grenquist, IND. ENG. CHEM., **20**, 1073 (1928).
(10) International Critical Tables, Vol. II, p. 272 (1927).
(11) *Ibid.*, p. 273.
(12) Kitchin, *Trans. Am. Inst. Elec. Eng.*, **48**, 495 (1929).
(13) Nordenson, *Kolloid-Z.*, **16**, 65 (1915).
(14) Nuttall, *Chemistry & Industry*, **47**, 1359 (1928).
(15) Smoluchowski, *Physik. Z.*, **6**, 529 (1905).
(16) Svedberg, "Colloid Chemistry," p. 238 (1928).
(17) Whitney and Blake, *J. Am. Chem. Soc.*, **26**, 1385 (1904).
(18) Wiegand, *Canadian Chem. J.*, **4** (1920).
(19) Williams and Kemp, *J. Franklin Inst.*, **203**, 35 (1927).

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Behavior of Various Clays with Crude and Reclaimed Rubber[1]

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The maximum and minimum variations produced by a large number of commercial clays in crude and reclaimed rubber have been determined. Their effect on both the uncured and the cured products have been studied. The chemical analysis gives but little information regarding their behavior in crude or reclaimed rubber. Clays show wide variation in plasticity, retentivity, and softness in crude and reclaimed rubber. They vary widely in their effect on the physical properties of crude and reclaimed rubber. Bomb aging is an important test for differentiating between various clays. In comparing samples of clays it is desirable to note their effect on the uncured as well as the cured properties of a compound.

THE emphasis which is placed on uniformity and ease of processing of rubber compounds makes it necessary to evaluate raw materials on the basis of both the uncured and cured properties of the compound. This study was made to show the variation produced by a large number of samples of commercial clays in crude and reclaimed rubber. It was observed that the properties of the uncured stocks in many cases showed much greater variation in hardness, feel, and processing than was predicted from the physical tests of the cured products. The influence of the clays in several cases was more marked in the uncured stock than in the cured compound.

[1] Received April 15, 1930. Presented before the Division of Rubber Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

It is the purpose of this paper to show the variations in crude and reclaimed rubber produced by the various clays on the basis of plasticity, retentivity, physical tests, oven and bomb aging, and chemical examination. The maximum and minimum limits as well as the average results of the samples of clay examined are graphically shown. A microscopic examination of the clays was made to show the relationship between particle size and physical tests of the crude or reclaimed rubber compounds. The results obtained bring out the maximum effects produced by clays and indicate the emphasis which should be placed on these effects in the examination and evaluation of a clay for rubber compounding.

Chemical Examination

Analysis of Clays

	Maximum	Minimum
Silica	94.2	37.46
Alumina	46.48	2.6
Iron oxide	3.0	0.1
Lime	2.2	None
Magnesia	3.24	Trace
Potash	1.35	0.13
Soda	1.63	0.05
Titania	1.56	0.44
Total alkalinity as Na_2CO_3	0.164	0.005
Total acidity as H_2SO_4	0.07	0.002

There was no relationship between iron oxide content and color of the clays. Neither was there any relationship between iron oxide content and oxygen bomb or oven aging in crude or reclaimed rubber. The samples containing the lowest and highest amounts of silica gave soft uncured stocks and the stress-strain curve of the cured products showed about the same reënforcing effect. Irrespective of the chemical composition of the clays, the behavior in rubber is largely determined by fineness of subdivision. The fact that some clays show acid reaction while others show an alkaline reaction should be kept in mind when using clay in different types of compounds. Some clays were found to give an acid reaction the highest of which gave an acidity of 0.07 per cent as sulfuric and others were decidedly alkaline in reaction, the highest of which contained 0.164 per cent alkali as sodium carbonate.

Microscopic Examination

Microscopic examination of the clays showed that there was a large variation in particle size from one sample to another. The minimum and maximum effects produced by the clays on the various physical tests may be predicted on the basis of particle-size measurements. The fineness of subdivision of a clay determines its influence on the properties of both the cured and uncured compounds. The finer the clay the greater is its stiffening power and reënforcing effect. A microscopic examination is one of the most important tests which can be applied to clays, since it enables one to make a quick classification of the material. The following table gives microscopic measurements of representative samples:

Maximum	Minimum	Average
μ	μ	μ
12	0.2	1
25	0.2	1.5
10	0.5	3
50	0.5	8
75	1.0	15

Reclaimed Rubber

Twenty parts of clay were refined with 80 parts of a standard alkali whole-tire reclaim. Four parts of sulfur were subsequently added on a mixing mill and slabs cured for 15, 30, 45, 60, and 75 minutes at 141.6° C.

Plasticity—Plasticity of the uncured stocks was determined on the Williams plastometer at 27° and 100° C. The clays are arranged in Figure 1 in order of decreasing plasticity at 100° C., the control containing no clay is the most plastic and No. 27 is the least plastic. It was found that the plastometer readings at either temperature failed to show the actual variations in consistency observed in the hand tests. The plasticities at 27° C. are lower than at

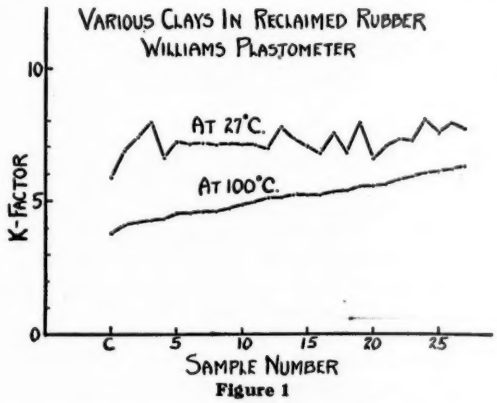

Figure 1

100° C., as would be expected, and are in less agreement with hand tests than the readings at 100° C. The plasticities at 27° C. show greater variation and a less gradual decrease in plasticity than at 100° C.

A comparison of the plasticities taken after 30 days with both the Goodrich and Williams plastometers shows a much wider variation in the case of the Goodrich plastometer. (Figure 2) The classification of the clays according to plasticity with the Goodrich plastometer corresponds very closely with the hand tests. A comparison of the original plasticity with that taken after 30 days with the Williams plastometer shows that there is a gradual "setting up" on standing. In the case of the Williams plastometer the lower the *K* value the softer is the stock, while with the Goodrich plastometer the lower the value the tougher is the stock. This should be kept in mind in observing Figure 2, since the units used for expressing plasticity do not correspond for the

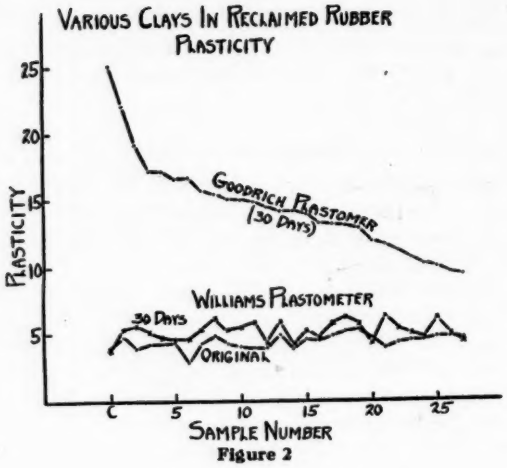

Figure 2

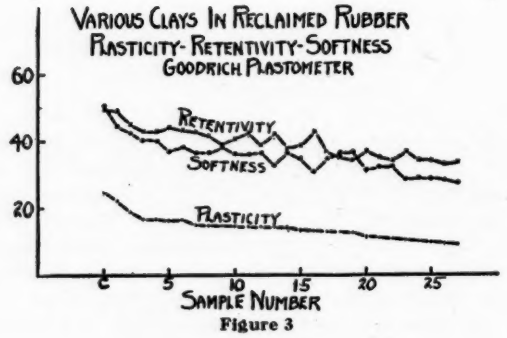

Figure 3

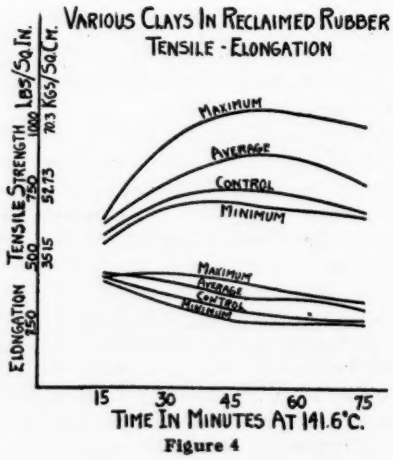

Figure 4

two plastometers. Plasticity as measured on the Goodrich plastometer takes into consideration both softness and retentivity, while on the Williams plastometer no account is taken of retentivity. The important fact brought out in this comparison is that the Goodrich plastometer is more sensitive in measuring differences in plasticity of clays in reclaimed rubber.

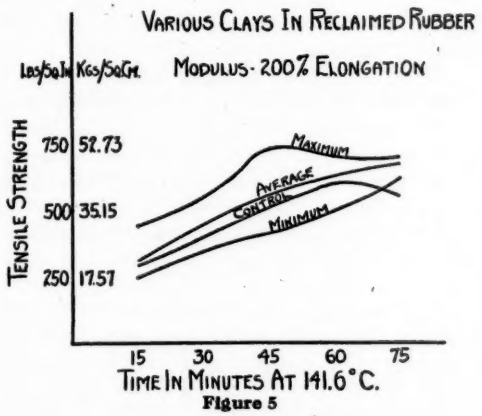

Figure 5

PLASTICITY—RETENTIVITY—SOFTNESS—A comparison of these properties taken on reclaimed rubber containing various clays indicates a diminishing value for retentivity and softness as the plasticity decreases. (Figure 3) The clay which shows the highest plasticity, retentivity, and softness has

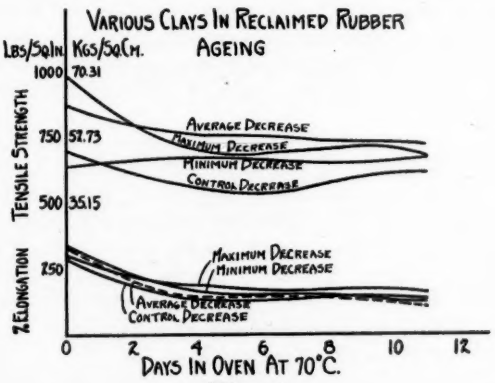

Figure 6

an average particle size of 15 microns, whereas the clay showing the lowest plasticity, retentivity, and softness has an average particle size of 1 micron. The coarser clays give softer stocks, because there is less rubber consumed than is the case with a fine clay.

TENSILE AND ELONGATION—Because of the number of

clays tested, it would have been both impractical and confusing to attempt to show individual curves for each clay. In order to simplify the presentation of results, it was therefore deemed advisable to show only maximum and minimum results which by comparison with the average and control (in which no pigment was added) will indicate clearly the trend of the intermediate curves. (Figure 4) The tensile varies from 74 kg. per sq. cm. on the maximum to 49 kg. per sq. cm. on the minimum, which shows even lower tests than are obtained in the case of the control which contains no pigment. An average of all the tests produces a curve which falls midway between that of the control and the maximum. The elongation curves fall in the same order as those of the tensiles but, as would be expected, do not show so much variation between the individual curves. The clay showing the highest tensile strength and elongation has an average particle size of 1 to 1.5 microns, whereas the sample showing the lowest tensile strength and elongation has an average particle size of 15 microns.

Modulus—Practically the same relationship holds true for the modulus, as was shown in the comparison of the tensile strength curves. The minimum curve falls below the control, although the average in this case is somewhat closer to the results obtained with the control. (Figure 5) The smaller the particle size the greater is the reënforcing effect.

Aging—Oven-aging tests were obtained using the 45-minute cure. (Figure 6) The maximum decrease in tensile strength is from 68.5 kg. per sq. cm. to 47.5 kg. per sq. cm. The average aging, however, is considerably better and the curve is, of course, higher than that obtained with the control or the minimum. The curve showing the minimum decrease has the least variation and is almost a straight line. The initial tensile strength, however, is considerably lower than in the case of the clay showing the maximum decrease on aging.

Bomb Aging—Samples of the 45-minute cure were aged for 48 hours in the oxygen bomb. The results shown on Figure 7 indicate good aging for most of the clays tested, since there is very little difference between the aging curves for the average and minimum decrease in tensile strength. This is also indicated on the graph showing elongations (Figure 8), since the curves showing maximum and minimum decrease in elongation also coincide.

Crude Rubber

Twenty-two samples of clay were incorporated into a compound of the following formula:

	Parts
Pale crepe	100
D. P. G.	1.57
Sulfur	3.91
Hvy. magnesium oxide	2.38
Zinc oxide	8.75
Clay	40.70
Stearic acid	1.54
	158.85

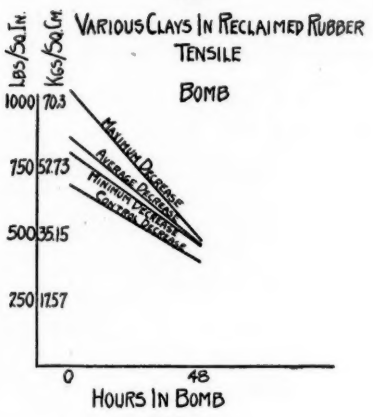

Figure 7

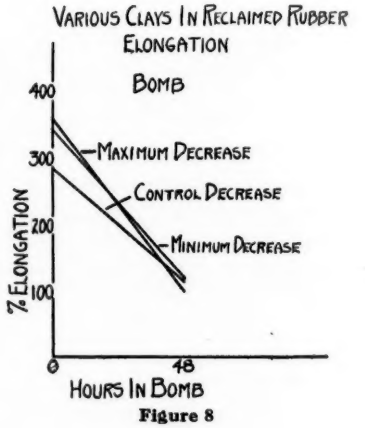

Figure 8

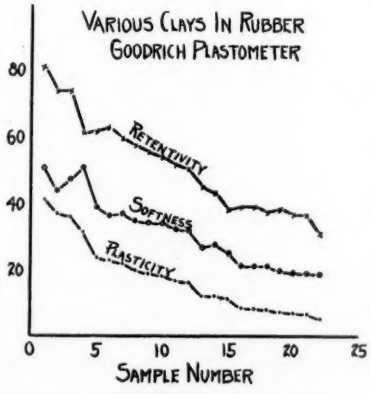

Figure 9

The compound was designed to give its maximum tensile strength in 30 minutes. Cures were made for 15, 30, 45, 60, 75, and 90 minutes at 141.6° C. This compound was chosen because the compounds in which clay is most generally used are designed for a short cure.

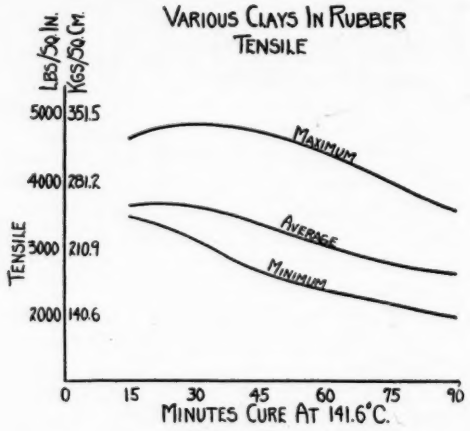

Figure 10

PLASTICITY—RETENTIVITY—SOFTNESS—Clays in a crude rubber compound give an uncured product showing a wide variation in plasticity, retentivity, and softness (Figure 9), as indicated by the Goodrich plastometer. Except for minor variations, the retentivity and softness curves follow the trend of the plasticity curve very closely.

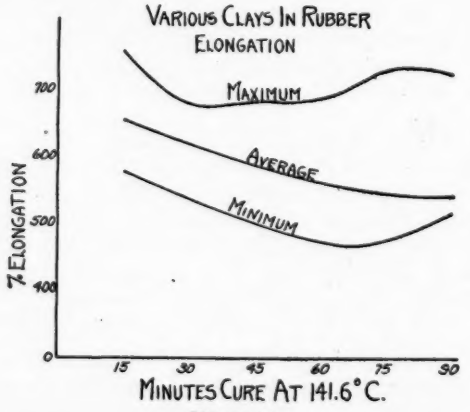

Figure 11

TENSILE STRENGTH AND ELONGATION—The variation in tensile strength shown in Figure 10 is very appreciable. The average tensile-strength curve corresponds more closely with the minimum curve. The elongation (Figure 11) of both the maximum and minimum curves shows reversion, whereas

the average curve does not. The finest clay gives the highest and the coarsest clay the lowest tensile strength.

STRESS STRAIN—Stress-strain curves of the 15-minute (Figure 12), 30-minute (Figure 13), and 75-minute (Figure 14) cures show but little variation in reënforcing effect. The average and maximum curves correspond very closely in all

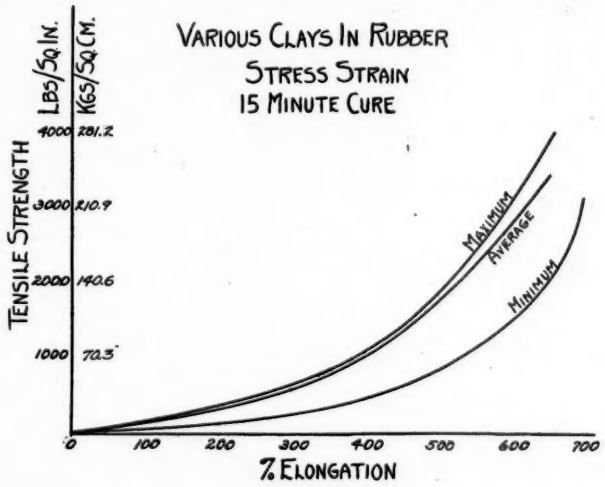

Figure 12

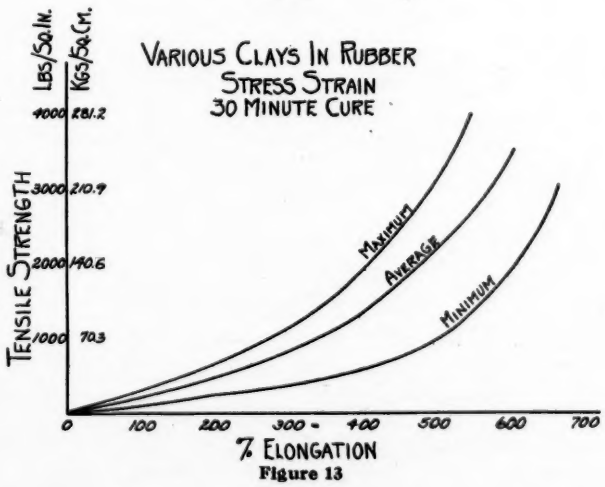

Figure 13

three cures. There are a few samples which show poor reenforcing properties. The minimum curve for the 75-minute cure (Figure 14) is low, owing to reversion. Here again the smaller the particle size the greater is the reënforcing effect of the clay.

RESISTANCE TO TEAR—The resistance to tear was measured both transversely and longitudinally and an average was

made of the two tests. The Winkelmann tear test was used. Compounds containing clay generally show low resistance to tear. Some clays (Figure 15) are much better than others, although the average of all clays is not much above the minimum. The smaller the particle size the better is the resistance to tear.

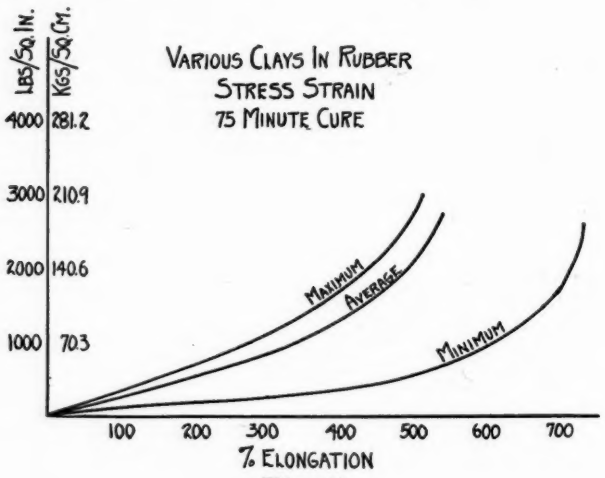

Figure 14

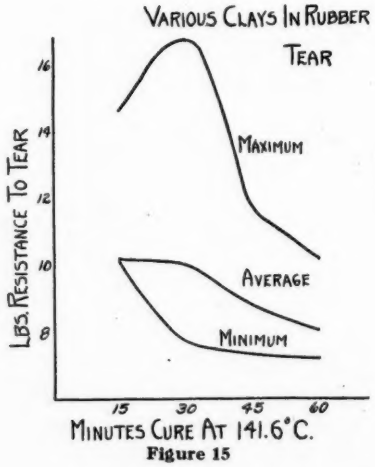

Figure 15

ABRASION LOSS—The resistance to abrasion as determined by the Grasselli abrador measures loss in cubic centimeters per horsepower hour. It is shown (Figure 16) that the average loss is but little more than was obtained with the best sample. Some samples of clay show poor resistance to abrasion compared with the average. Owing to inconsistent

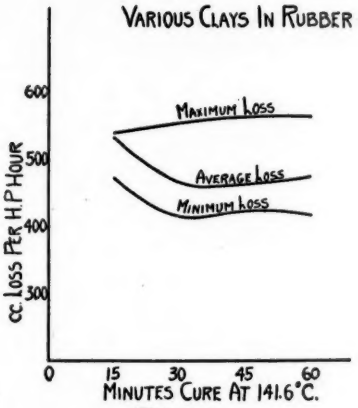

Figure 16

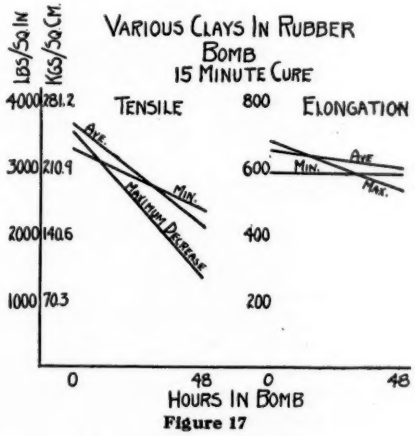

Figure 17

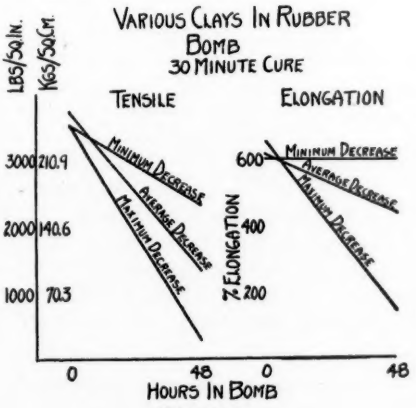

Figure 18

results, it is impossible to draw any conclusions regarding the effect of particle size on resistance to abrasion.

Bomb Aging—Samples of the 15- and 30-minute cures were aged in the oxygen bomb for 48 hours. (Figure 17) The variation in the decrease in tensile strength and elongation on the 15-minute cure is very slight and there is hardly any difference between the average and minimum decrease curves. The 30-minute cure shows the importance of bomb aging, because on this cure there is considerably more variation between the minimum and maximum decrease curves for tensile strength. (Figure 18)

Conclusions

1—The chemical analysis of clays gives but little information regarding their behavior in crude or reclaimed rubber. Acidity or alkalinity should be determined for effect on rate of cure. Color of the clay is no criterion of its purity.

2—Clays show wide variations in plasticity, retentivity, and softness in crude and reclaimed rubber.

3—Commercial clays vary widely in their effect on the physical properties of crude and reclaimed rubber. In general, the effect of the clays is the same in reclaimed as in crude rubber. There is not quite the percentage variation in tensile strength in reclaimed rubber that there is in crude rubber. The alkalinity of the reclaim may have decreased the variation.

4—Bomb aging is an important test for differentiating between various clays.

5—The uncured as well as cured properties of a compound should be noted in compounding and processing various samples.

6—Microscopic examination of clays makes it possible to predict their effect on the uncured and cured properties in both crude and reclaimed rubber.

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Method of Making Micro-Sections of Rubber Stocks[1]

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THE possibility of seeing pigment particles in a rubber stock has always been a desire of rubber chemists. There has been a natural belief that if the particles in rubber could actually be observed with a microscope more could be learned about their action and properties. The main difficulty in attaining this end lies in the preparation of sufficiently thin sections. For clear observation of highly loaded gas-black stocks the sections must be less than 1 micron thick. For bright-field work with light-colored or colorless pigments, such as litharge and zinc oxide, the sections may be somewhat thicker. However, if the examination is to be made with dark-field illumination the sections for even the colorless pigments must again be very thin.

Several methods have been proposed and utilized for making thin sections, and the names of Dannenberg (*2*), Depew (*3*), Green (*4*), Grenquist (*5*), Hauser (*7*), Moore (*11*), Pohle (*9*), Ruby (*3*), Spear (*11*), and Walton (*12*) are identified with the skilful manipulation which is necessary for achieving the desired result. There have been many other workers in this field, including Weber (*13*), Breuil (*1*), Loewen (*8*), Regnaud (*10*), and Hardman (*6*).

The method to be described was developed in this laboratory in 1926. It has been used continually since that time and has proved valuable in the study of rubber compounds and pigments. While it bears a slight similarity to some of the other methods, it has certain unique and distinct advantages of its own.

[1] Received April 15, 1930. Presented before the Division of Rubber Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

Previous methods have required the use of elaborate equipment, usually of a microtome, and have been laborious and time-consuming. In order to cut a thin section of rubber with a microtome knife, it is first necessary to make the rubber

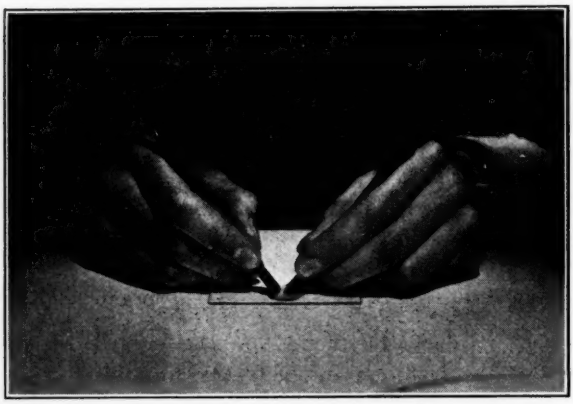

Figure 1—Scalpel Handles as Used for Cutting Rubber Micro-Sections

stock semi-hard, either by curing or freezing. The disadvantage of curing is that the pigment particles or their dispersion in the rubber may be altered. Freezing with liquid

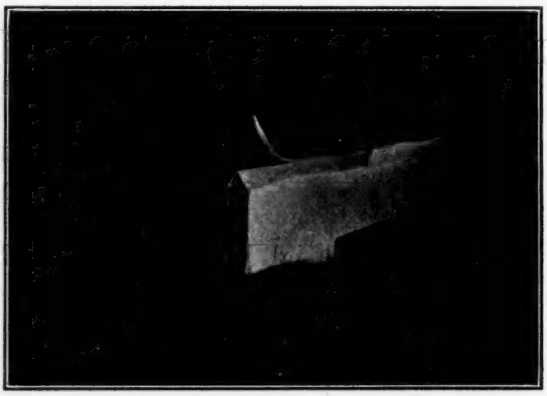

Figure 2—Sliver of Rubber from Which Micro-Section Is Cut

air or with carbon dioxide and ether and cutting sufficiently thin sections is rather laborious, but this method has the very great advantage of retaining the pigment particles without change in their original position.

Method

By the method developed in this laboratory thin sections of either cured or uncured stocks can easily be made in a few minutes with very simple tools. The necessary equipment consists of a microscope slide, a cover glass, a small piece of

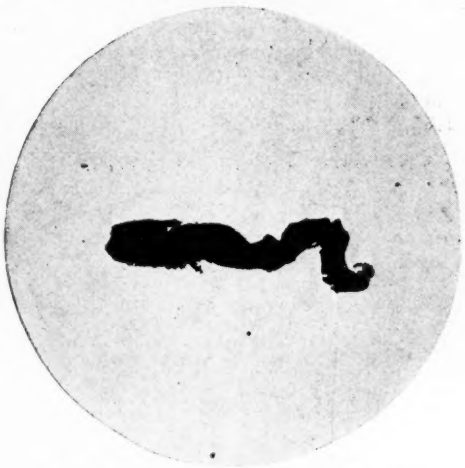

Figure 3—Unsqueezed Section of Tread Stock. × 100

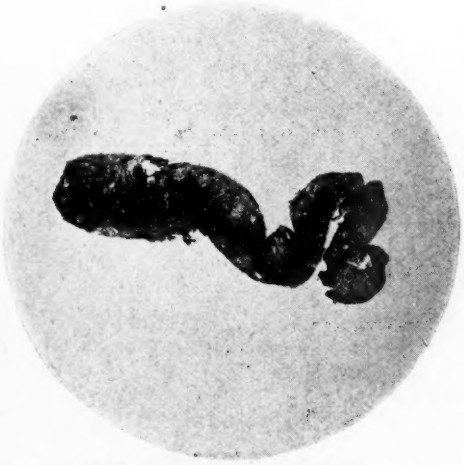

Figure 4—Same Section as in Figure 3, after Squeezing. × 100

beeswax or rosin, a small pair of dissecting scissors, and two suitably shaped pieces of wood. The latter may consist of any flat, blunt sticks, such as the handle of a small scalpel. These are illustrated in Figure 1. A triangular ridge is first

cut on the edge of the piece of stock to be examined. Then with the scissors a tiny sliver of rubber is cut from the crest of this ridge and the very tip of this sliver is cut off for use. In Figure 2, illustrating the method of cutting, the size of the sliver has been exaggerated. The final piece should be barely

Figure 5—A Portion of Section Shown in Figure 4. × 750

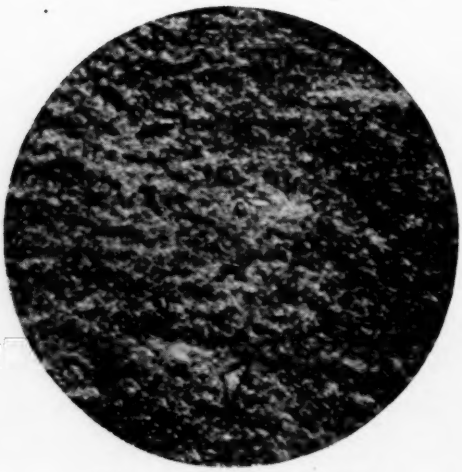

Figure 6—A Portion at × 1500

visible to the naked eye, and it is often desirable to use a low-power Greenough microscope to observe the cutting. Great care must be used in the cutting, because this piece must be so small that subsequent squeezing will not cause extreme distortion of agglomerates or destroy the relation of one particle to another.

This minute piece is carefully laid in the center of a small drop of rosin or beeswax which has been previously melted on the slide. The rosin is remelted and the cover glass is placed over the pool of liquid containing the sample. The

Figure 7—Thermax in Rubber, Bright-Field Illumination. × 1000

Some zinc oxide is also present

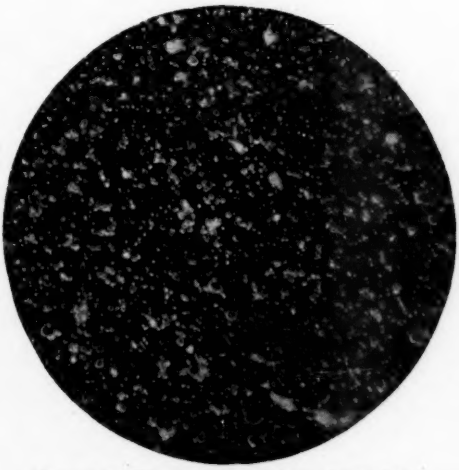

Figure 8—Thermax in Rubber, Dark-Field Illumination. × 1000

Same field as in Figure 7

rubber is now squeezed out thin by applying pressure on the cover glass with the wooden strips and held in this position until the rosin hardens and the thin section is permanently held in place. It is inadvisable to press directly over the piece

of rubber, because the cover glass is liable to spring away from the section when the pressure is removed, thereby introducing a zone of low refractive index into the system and decreasing the resolving power of oil immersion objectives.

The size and character of an unsqueezed piece of cured

Figure 9—Kadox in Rubber. × 1500

Figure 10—Channel Gas Black, Poorly Dispersed in Rubber. × 1000

tread stock carrying 25 per cent of gas black is shown in Figure 3 at 100 diameters, while the same sample after squeezing is illustrated in Figure 4 at the same magnification, a portion of it in Figure 5 at 750, and in Figure 6 at 1500 diameters. These illustrations show that by his method it is possible to

make sections less than 1 micron in thickness, even of stiff stocks.

For satisfactory observation with dark field, not only is a thinner section required than with bright field, but also the concentration of pigment must be less. The blackness of

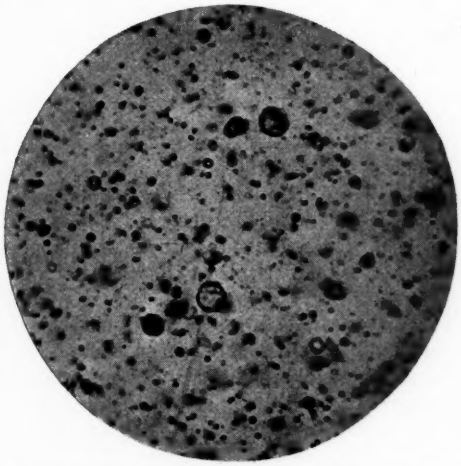

Figure 11—Sublimed Litharge in Rubber. × 1000

Figure 12—American Process Zinc Oxide in Rubber. × 1000

background and sharpness of contrast so necessary for clear observation with dark field are lost if the field contains too many particles. This principle is illustrated by Figures 7 and 8, where the same field of a section of stock containing about 12 per cent of Thermax has been photographed with

bright-field and dark-field illumination. While the pictures do not show a great difference, visual examination of this section in the microscope gives the impression of a much larger number of particles in the dark-field view.

With pigments of smaller particle size, such as Kadox and channel gas black, the satisfactory use of dark field usually requires an exceedingly low concentration. In Figure 9, which shows an excellent section for observation, the stock contains only 0.3 per cent of Kadox.

Applications

It is not possible to describe here all the varied applications of this method of making rubber sections. One application is suggested in Figure 10, where poor dispersion of gas black in a rubber stock may readily be observed.

Figure 11, showing sublimed litharge in uncured stock, illustrates the advantage of this method of sectioning rubber over a curing method. The particles of litharge have retained their usual light yellow color, whereas if cure had occurred the particles would have turned brown or black.

Figure 12 shows again that a section can easily be made with the pigment particles lying in practically one plane. It is a picture of American process zinc oxide at 1000 diameters, using dark-field illumination.

The method was developed for the study of pigments in rubber stocks. It should be pointed out, however, that rubber is an excellent medium in which to examine pigments. Most fine, solid particles are easily dispersed in rubber. Rubber is rigid enough to prevent Brownian movement of particles dispersed in it, and yet sufficiently plastic to be easily deformed. Its refractive index (approximately 1.517) differs enough from that of most pigments so that they can be distinctly seen when dispersed in rubber. As a dispersing medium, however, rubber has the disadvantage of not being optically empty, but this difficulty is not very troublesome except in the case of pigments of low visibility. With very low concentrations of channel black, for example, using dark field, it is almost impossible to distinguish foreign particles in the rubber itself from the particles of black.

This method of making sections is recommended as a quick and convenient means of preparing rubber stocks for the microscopic observation of pigments in rubber.

Acknowledgment

The writer wishes to acknowledge the valuable aid given by Frank H. Roninger, Jr., in the preparation of this paper.

Literature Cited

(1) Breuil, *Caoutchouc & gutta-percha*, **2**, 82, 118, 158, 197 (1905).
(2) Dannenberg, *Kautschuk*, **3**, 104, 128 (1927).
(3) Depew and Ruby, J. IND. ENG. CHEM., **12**, 1156 (1920).
(4) Green, *Ibid.*, **13**, 1130 (1921).
(5) Grenquist, *Ibid.*, **20**, 1073 (1928); **21**, 665 (1929).

(6) Hardman, *India Rubber World*, **68**, 711 (1923).
(7) Hauser, Colloid Symposium Monograph, Vol. VI, p. 207 (1928).
(8) Loewen, *Gummi-Ztg.*, **27**, 1301 (1913).
(9) Pohle, *Kolloid-Z.*, **38**, 75; **39**, 1 (1926); *Z. wiss. Mikroskop.*, **44**, 183 (1927); *Gummi-Ztg.*, **42**, 2687 (1928).
(10) Regnaud, *Chimie & industrie*, **18**, 397 (1927).
(11) Spear and Moore, IND. ENG. CHEM., **17**, 894, 936 (1925).
(12) Walton, *Ibid.*, Anal. Ed., **1**, 106 (1929).
(13) Weber, "The Chemistry of India Rubber," pp. 41, 110, London, 1919.

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Effect of Pigmentation on the Work of Retraction of Rubber Compounds[1]

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THE reënforcement of rubber by pigments has been studied by a number of investigators (*4*, *5*) by considering the effect of pigmentation on the extension stress-strain curves and on the areas enclosed between these curves and the elongation axes, which areas are a measure of the work of extension. (Figure 1) These investigations, in conjunction with other data, have developed two opinions concerning the mechanism of reënforcement; one (*2*), that reënforcement is caused by a bond between the rubber and the pigment particles; the other (*3*), that reënforcement is primarily a function of the particle size of the pigment and that the bond is of secondary importance.

The work cited above shows that pigments exert different effects on work of extension, and it has consequently been assumed that they would have somewhat similar effects on work of retraction as measured by the areas enclosed between the retraction curves and the elongation axes. (Figure 1)

The data assembled in this report, however, show that work of retraction from a given elongation is much more independent of the kind or amount of the pigment used. For example, if several pigments and several volume loadings are chosen at random, it will be found that a 5-volume carbon black, a 10-volume Kadox, a 20-volume clay, and a 30-volume XX red zinc oxide stock will all have approximately the same work of retraction from any elongation which is common to all the compounds, although the work

[1] Received April 15, 1930. Presented before the Division of Rubber Chemistry at the 79th Meeting of the American Chemical Society, Atlanta, Ga., April 7 to 11, 1930.

of extension to the same elongation for these compounds is quite widely different.

It follows that the retraction curves for two compounds differing only in the kind and amount of pigment used must cross in returning from the same elongation, as is illustrated in Figure 2. The stiffer the stress-strain curve on extension, the lower is the retraction curve when returning to zero stress. The data further show that work of retraction does depend, in some measure at least, upon the quality and condition (state of cure) of the rubber used.

The interpretation of this behavior involves many considerations, and though it undoubtedly has considerable bearing on the theory of reënforcement, any discussion of this aspect of the work will be reserved for a future paper.

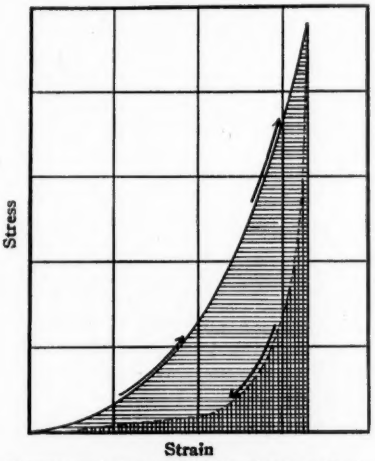

Figure 1—A Typical Rubber Stress-Strain Extension and Retraction Curve

The entire area between the extension curve (heavy line) and the elongation axis is a measure of the work of extension. The cross-hatched portion between the retraction curve (dotted line) and the elongation axis is a measure of the work of retraction.

Conditions of Experimental Work

In carrying out this work it was necessary to take several important factors into consideration:

(1) The pigments chosen should be representative of a wide range of particle size and behavior in rubber compounds. These pigments were Red Label Kadox, carbon black, XX red zinc oxide, clay, and ground barytes. Three of these are high-grade reënforcing pigments and the other two are fillers. They were used in concentrations of 5–10–20–30–40 and 50 volumes of pigment to 100 volumes of rubber.

(2) The pigments should be used in a base compound which would be fairly representative of commercial practice, and which would contain sufficient sulfur to overcome any tendency towards reversion which might be manifest if a smaller amount

were used, due to the chemical combinations of the sulfur with some of the pigments. The base compound selected was:

Pale crepe	920	100 volumes
Sulfur	55	6% on rubber by wt.
Diphenylguanidine	9.2	1% on rubber by wt.
Mineral Rubber	4.6	0.5% on rubber by wt.
Stearic acid	2.3	0.25% on rubber by wt.
Red Label Kadox	168	3 volumes

(3) The milling practice should be such as to preclude any possibility of pre-vulcanization set-up and to insure the same treatment for every compound. To this end the above base compound with the sulfur omitted was master-batched on a 16 × 42 inch mill and the pigments were later added on a 6 × 12 inch laboratory mill. The sulfur was added last. All milling was carried out with the rubber at 70° C.

(4) The vulcanization periods should be such as to have every compound at a comparable cure. With pigments of such widely different characteristics it was impractical to choose any

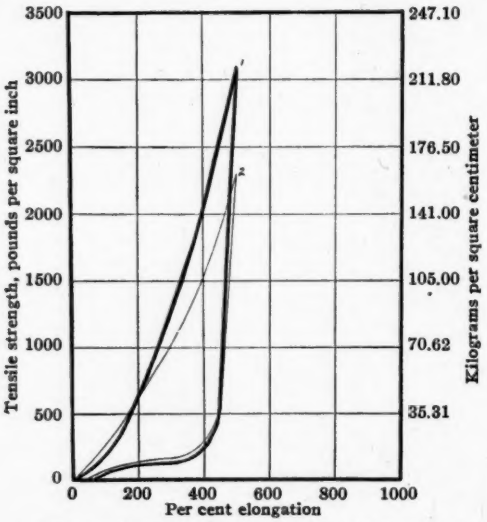

Figure 2—Crossing of Retraction Curves of Two Compounds, One Containing 20 Volumes of Carbon Black (1), and the Other Containing 20 Volumes of XX Red Zinc Oxide (2)

one time which would be satisfactory for all stocks. It was decided to choose that cure which had the highest work of extension after 14 days' aging in a Geer oven at 70° C. Figure 3 illustrates the method. Work of extension was plotted against time of cure for all the Red Label Kadox stocks after they had been aged for 14 days at 70° C. The dotted line traces the shift of time to the comparable cure as the pigment concentration increases. The time to the comparable cures for all compounds is shown in Table I.

There are various ways of determining time to the comparable cure, each of which has its advantages and disadvantages. One method, which is independent of aging, is to choose that time at which the compound reaches its highest initial tensile strength. If that had been done in this case, the comparable cures would not have differed appreciably from those found, as is shown in Table I.

The times to comparable cure are in line with general ex-

perience; increasing amounts of carbon black retard the cure through the ordinary compounding range (up to 20 volumes of pigment), and Kadox causes a considerable acceleration.

Table I—Time Necessary for Compounds to Reach Their Comparable Cures When Vulcanized at 30 Pounds (2 atm.) Steam Pressures (134.5° C.)

Volumes of Pigment	XX Red Zinc Oxide	Carbon Black	Red Label Kadox	Clay	Ground Barytes
	Minutes	*Minutes*	*Minutes*	*Minutes*	*Minutes*
0	60 (60)	60 (60)	60 (60)	60 (60)	60 (60)
5	60 (60)	70 (65)	65 (60)	70 (60)	42 (60)
10	63 (67)	70 (70)	57 (50)	70 (60)	43 (60)
20	70 (70)	70 (70)	38 (35)	53 (60)	51 (50)
30	80 (80)	55 (70)	27 (30)	48 (50)	53 (50)
40	84 (90)	42 (60)	16 (20)	43 (40)	59 (60)
50	86 (90)	40 (40)	5 (7)	40 (40)	60 (60)

(The figures in parentheses are time to the tensile peak before aging.)

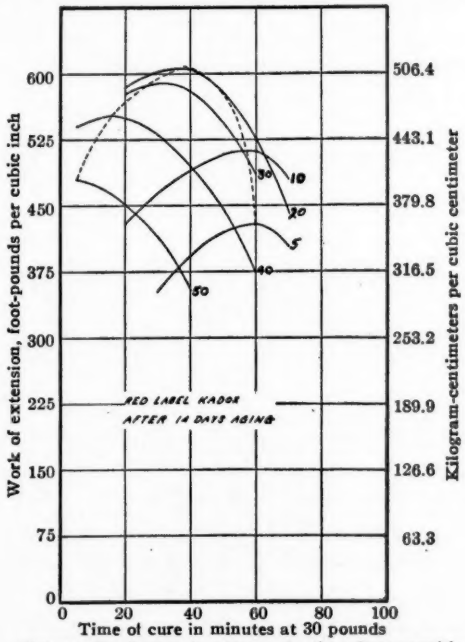

Figure 3—Determination of the Comparable Cures for a Range of Volume Loadings of Red Label Kadox

The smooth dotted line connects the approximate points of highest work of extension after accelerated aging. The intersection of this line with the solid curves determines the time to the comparable cures more accurately than could be done by inspection of the solid curves alone.

The retraction curves were taken on the first cycle so that they would be comparable to the considerable amount of data already published on work of extension.

Unpublished data by W. W. Vogt, of the Goodyear Tire & Rubber Company, have shown that the results are decidedly different if different conditions of test are used. Vogt measured the rebound of a weighed pendulum from the surface

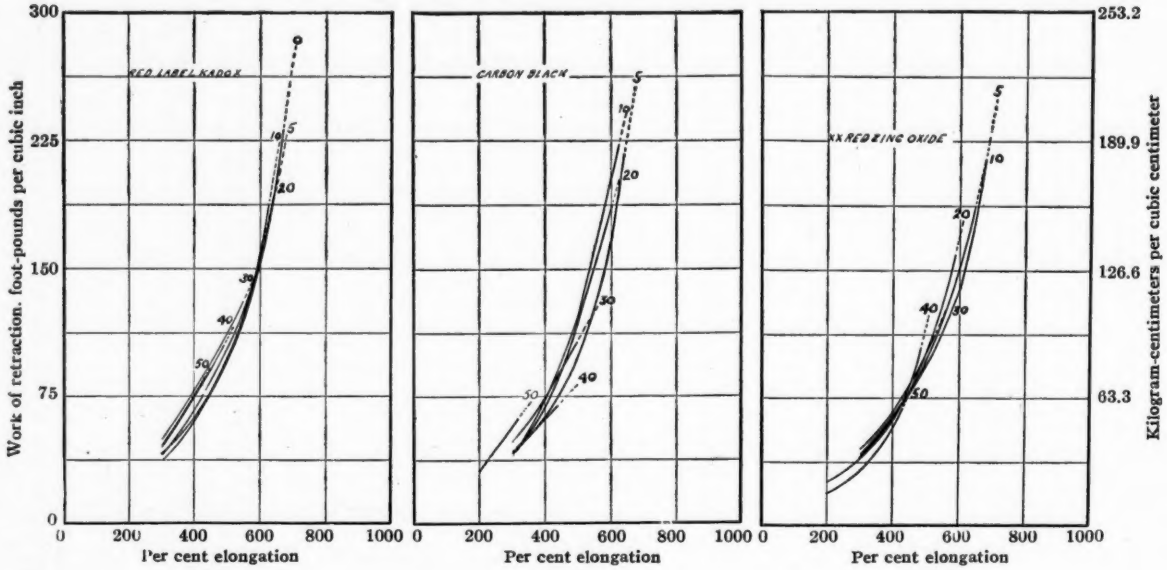

Figure 4 Figure 5 Figure 6

Work of Retraction for a Range of Volume Loadings of Various Pigments
(Numbers on curves represent volumes of pigment)

of rubber compounds. The length of the swing was adjusted so that equal penetration of the weight into the sample was secured. It was found that the energy of rebound, which might be comparable to work of retraction, was dependent upon the kind and amount of pigment used. This should not be unexpected, however, because the conditions of test in the two cases were radically different. Energy of rebound is essentially a very rapid test under very nearly adiabatic conditions. Work of retraction is a test which is, comparatively, very slow and the conditions are much more nearly isothermal.

Vogt further found that the state of cure of the com-

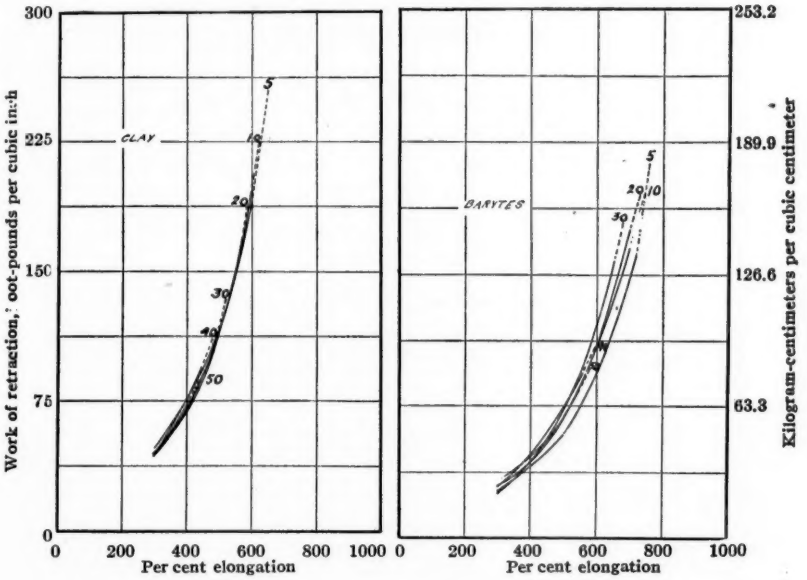

Figure 7 Figure 8

Work of Retraction for a Range of Volume Loadings of Various Pigments
(Numbers on curves represent volumes of pigment)

pound had very little effect on energy of rebound; this being in line with published work by Williams (*6*).

The complexity of the problem is further shown by the fact that state of cure has a decided effect when a large block of rubber is tested with the Whitney rebound tester.

Experimental Procedure

Work of retraction for these compounds at the cures mentioned above was determined by measuring the areas enclosed between the retraction curves and the elongation axes at elongations starting at 300 per cent and increasing by 100 per cent to as near the breaking point of the piece as possible. The measurements were then calculated as foot-

pounds per cubic inch or kilogram centimeters per cubic centimeter. Ultimate work of retraction at break was determined by extrapolating the work of retraction-elongation curves to the breaking elongation of the compound. For every different elongation it was necessary, of course, to employ unused test pieces.

The extension and retraction stress-strain curves were made

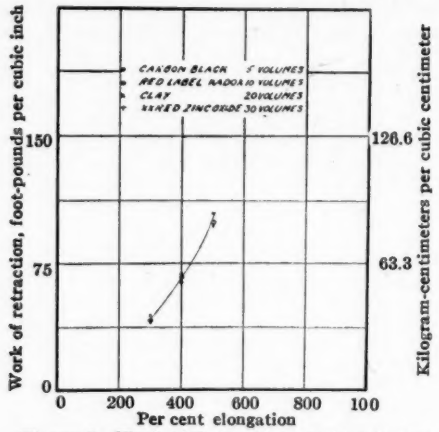

Figure 9—Work of Retraction at 300, 400, and 500 Per Cent for a 5-Volume Carbon Black, a 10-Volume Kadox, a 20-Volume Clay, and a 30-Volume XX Red Zinc Oxide Stock

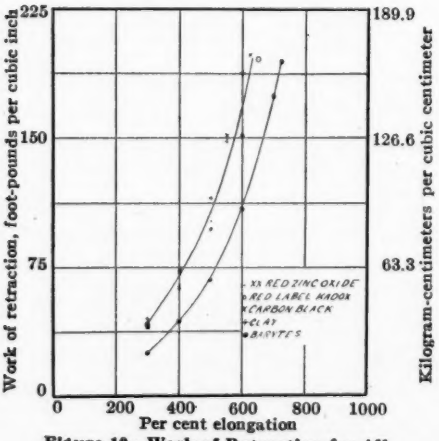

Figure 10—Work of Retraction for All 20-Volume Compounds

according to the standard A. S. T. M. testing methods (*1*).

The test pieces were stretched on a regular rubber-testing machine. The jaws separated at a speed of 20 inches (51 cm.) per minute until the required elongation was obtained. A throw of a switch immediately reversed the jaws and they returned with the same speed at which they had separated.

Results

The data are given in Figures 4 to 8. These curves show that work of retraction from any given elongation is practically independent of the kind or amount of pigment used with the exception of the barytes compound. As illustra-

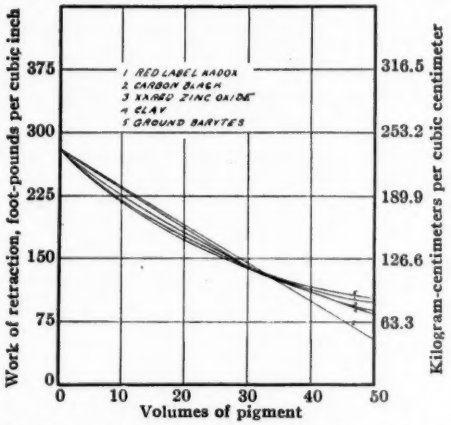

Figure 11—Effect of Pigmentation on Work of Retraction Calculated to Breaking Elongation

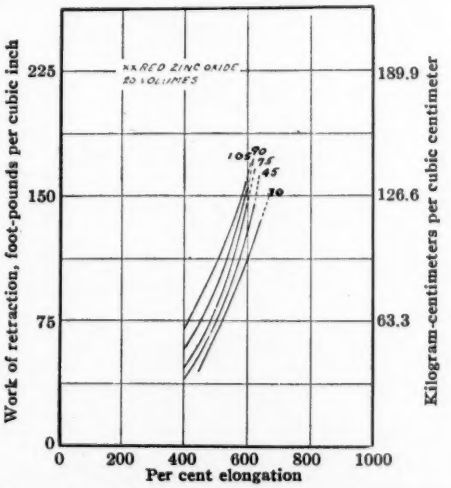

Figure 12—Effect of Cure on Work of Retraction
(The numbers on the curves represent time of cure in minutes)

tions of these facts, Figures 9 and 10 are presented. All points on the curve in Figure 9 are very close, in spite of the fact that they represent four different pigments and four different volume loadings. In Figure 10 the barytes compound is the only one which does not fall on the general

curve. This may be explained by the fact that vacuoles were formed during extension, and that consequently the rubber was under less strain than it was in the other compounds.

When ultimate work of retraction, calculated to the breaking elongation, is plotted against volumes of pigment as in Figure 11, it is seen that it also is virtually independent of the kind of pigment used. It is, however, dependent upon the ultimate elongation of the compounds which are greatly influenced by the amount of pigment used.

That work of retraction and ultimate work of retraction are influenced by the condition, or state of cure, of the rubber in the compound, can be seen by an examination of Figure 12. For obtaining these data the 20-volume XX red zinc oxide compound was used, cured for 30, 45, 75, 90, and 105 minutes at 30 pounds. Work of retraction at elongations short of break has increased for every increase in time of cure. Ultimate work of retraction has also increased to a point beyond the optimum, which occurred in 70 minutes, and has then started to decrease.

Literature Cited

(1) American Society for Testing Materials, Specifications for Testing Rubber Products, D15–24 (1927).
(2) Blake, IND. ENG. CHEM., **20**, 1084 (1928).
(3) Depew, *Rubber Age (N. Y.)*, **24**, 378 (1929).
(4) Lunn, *Trans. Inst. Rubber Ind.*, **4**, 396 (1929).
(5) Wiegand, *Can. Chem. J.*, **4**, 160 (June, 1920).
(6) Williams, IND. ENG. CHEM., **21**, 872 (1929).

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